QAPP Addendum

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To: Susan Morales and Donald Brown (USEPA)

From: Joel Hecker, LG (WA, KY, IN, NC, SC)

Cc: Mike Reid (City of Olympia)

Date: May 27, 2020

Subject: Generic QAPP Addendum for Sediment Sampling
Olympia Washington USEPA Brownfield Assessment Grant (BF01J66201)

The purpose of this Quality Assurance Project Plan (QAPP) Addendum is to present additional information that was not included in the generic QAPP for the City of Olympia's (the City's) brownfield assessment grant. The generic QAPP was approved by the United States Environmental Protection Agency (USEPA) on March 16, 2020. The information included in the generic QAPP remains valid. This QAPP addendum details laboratory analytical methods, reporting limits, quality control (QC) limits, sample containers, holding times, and preservation and storage requirements for sediment samples collected with funding from the City's brownfield assessment grant.

Chemical Analyses

Consistent with the generic QAPP, sediment samples will be submitted to Libby Environmental (Libby), who will either analyze samples in house, or will subcontract analyses to Fremont Analytical (Fremont), Analytical Resources, Inc. (ARI), or Materials Testing & Consulting. The specific analyses and conventional parameters to be measured by each laboratory, sample preparation methods, analytical methods, method detection limits (MDLs), target reporting limits (RLs), QC limits, and applicable regulatory criteria are presented in Table 1. Actual sample RLs may vary due to analytical dilutions, percent solids, sample volumes used for analysis, and matrix interferences.

The laboratories participating in sediment projects are accredited by the Washington Department of Ecology (Ecology) for all analytical methods to be used for sediment projects, and have instituted internal quality assurance/quality control (QA/QC) plans accordingly. Attachment 1 provides the Ecology certification for Materials Testing & Consulting and standard operating procedures for the methods discussed in this QAPP addendum that have not already been submitted in the generic QAPP (i.e., conventionals listed in Table 1). Analyses will be required to conform to accepted standard methods and internal QA/QC checks prior to final approval.

Comparison to Sediment Management Standards

The results will be compared to Ecology's Sediment Management Standards (SMS) Sediment Quality Standards (SQS; Washington Administrative Code [WAC] 173-204-320) and Sediment Impact Zone Standards (SIZmax; WAC 173-204-420). A comparison of the SQS and SIZmax criteria to the MDLs and RLs is shown on Table 1. All reasonable means, including additional cleanup steps and method modifications, will be used to achieve sample MDLs and RLs at or below the associated SQS and SIZmax criterion.

MDLs and/or RLs for all listed chemicals are below SMS criteria based on dry weight and organic carbon (OC) within the applicable range of organic carbon content (0.5 to 3.5 percent). Undetected chemicals with MDLs that exceed the SQS criteria will be considered SMS exceedances.

Sample Containers, Holding Times, and Preservation and Storage Requirements

Sample containers, holding times, and preservation and storage requirements for sediment sample analyses are shown on Table 2.

Enclosures

Table 1	Chemical Parameters, Laboratory QC Limits, and SMS Criteria
Table 2	Sediment Sample Analysis Summary, Preservation, Sample Container, and Holding Times
Attachment 1	Laboratory Standard Operating Procedures and Accreditations

QAPP Addendum Approval

The QAPP Addendum for sediment sampling has been approved by the following Project Team members:

Name and Role	Signature and Date
Susan Morales USEPA Project Manager	6.8.20
Donald M. Brown USEPA Brownfields QA Reviewer	6/8/2020
Mike Reid City of Olympia Grantee Project Manager	Mike Reid 06/02/2020
Joel Hecker, LG PIONEER Project Manager	5/27/2020
Angela Noyan PIONEER QA Manager	5/27/2020
Kody Eley Libby Environmental Laboratory Director	Kody Eley 5/27/2020
Mark Weidner Analytical Resources, Inc. Laboratory Director (subcontractor to Libby)	5/27/2020
Medhanie Tecle Materials Testing & Consulting Laboratory Director (subcontractor to Libby)	Medhanie Tecle 05/27/2020

Tables

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Table 1: Chemical Parameters, Laboratory QC Limits, and SMS Criteria

Parameter	Laboratory	Analysis Method	MDL	RL	Duplicate RPD	Matrix Spike		Blank Spike/ LCS		Ecology Sediment Management Standards[1]	
						%R	RPD	%R	RPD	SQS	SIZmax
Conventionals											
Grain size (%)	Materials Testing & Consult.	PSEP	–	0.1		--	--	--	--	–	–
Total organic carbon (%)	Fremont	9060	0.0075	0.075	30	38.5-146	20	70-131	20	–	–
Total solids (%)	ARI	PSEP	0.04	0.04	20	--	--	--	--	–	–
Total volatile solids (%)		PSEP	0.01	0.01	20	--	--	--	--	–	–
Ammonia (mg/kg)		PSEP/Plumb	0.4	5.0	20	75-125	20	90-110	20	–	–
Total sulfides (mg/kg)		PSEP/9030	1.0	1.0	20	75-125	20	75-125	20	–	–
Metals (mg/kg)			mg/kg dry wt							mg/kg dry wt	
Arsenic	Fremont	6020B	0.078	0.3	20	75-125	20	80-120	20	57	93
Cadmium		6020B	0.00098	0.2	20	75-125	20	80-120	20	5.1	6.7
Chromium		6020B	0.026	0.1	20	75-125	20	80-120	20	260	270
Copper		6020B	0.027	0.2	20	75-125	20	80-120	20	390	390
Lead		6020B	0.0035	0.2	20	75-125	20	80-120	20	450	530
Mercury		7471B	0.019	0.5	20	75-125	20	80-120	20	0.41	0.59
Silver		6020B	0.0013	0.1	20	75-125	20	80-120	20	6.1	6.1
Zinc		6020B	0.061	0.5	20	75-125	20	80-120	20	410	960
Non-Ionizable Organic Compounds			mg/kg dry wt							mg/kg OC	
LPAH[2]	Fremont	8270D	–	0.05	50	19-118	50	40-115	30	370	780
Naphthalene		8270D	0.009	0.05	50	19-118	50	40-115	30	99	170
Acenaphthylene		8270D	0.0058	0.05	50	16-134	50	44-127	30	66	66
Acenaphthene		8270D	0.017	0.05	50	18-132	50	47-130	30	16	57
Fluorene		8270D	0.012	0.05	50	20-133	50	53-134	30	23	79
Phenanthrene		8270D	0.016	0.05	50	24-129	50	47-131	30	100	480
Anthracene		8270D	0.091	0.05	50	16-137	50	45-122	30	220	1200
2-Methylnaphthalene		8270D	0.0077	0.05	50	14-132	50	40-121	30	38	64
HPAH[3]		8270D	--	0.05	50	5-143	50	41-129	30	960	5300
Fluoranthene		8270D	0.0072	0.05	50	24-141	50	51-135	30	160	1200
Pyrene		8270D	0.0056	0.05	50	26-138	50	51-135	30	1000	1400
Benzo(a)anthracene		8270D	0.011	0.05	50	15-142	50	49-140	30	110	270
Chrysene		8270D	0.014	0.05	50	14-134	50	54-138	30	110	460
Total benzofluoranthenes[4]		8270D	0.013	0.05	50	6-148	50	37-148	30	230	450
Benzo(a)pyrene		8270D	0.012	0.05	50	5-143	50	41-129	30	99	210
Indeno(1,2,3-c,d)pyrene		8270D	0.0133	0.05	50	5-139	50	32-135	30	34	88
Dibenzo(a,h)perylene		8270D	0.016	0.05	50	5-138	50	30-136	30	12	33
Benzo(g,h,i)perylene		8270D	0.0099	0.05	50	5-130	50	25-140	30	31	78
1,2-Dichlorobenzene		8270D	0.01	0.075	50	22-105	50	34-102	30	2.3	2.3
1,4-Dichlorobenzene		8270D	0.0069	0.075	50	21-102	50	31-99	30	3.1	9
1,2,4-Trichlorobenzene		8270D	0.0091	0.075	50	21-112	50	39-111	30	0.81	1.8

Table 1: Chemical Parameters, Laboratory QC Limits, and SMS Criteria

Parameter	Laboratory	Analysis Method	MDL	RL	Duplicate RPD	Matrix Spike		Blank Spike/ LCS		Ecology Sediment Management Standards[1]	
						%R	RPD	%R	RPD	SQS	SIZmax
Hexachlorobenzene	Fremont	8270D	0.02	0.075	50	16-130	50	52-145	30	0.38	2.3
Dimethyl phthalate		8270D	0.01	0.1	50	18-142	50	45-134	30	53	53
Diethyl phthalate		8270D	0.012	0.1	50	23-144	50	55-137	30	61	110
Di-n-butyl		8270D	0.011	0.1	50	27-145	50	47-138	30	220	1700
Butyl benzyl phthalate		8270D	0.0099	0.1	50	32-157	50	50-135	30	4.9	64
Bis(2-ethylhexyl) phthalate		8270D	0.016	0.1	50	5-153	50	31-128	30	47	78
Di-n-octyl phthalate		8270D	0.011	0.1	50	5-161	50	33-126	30	58	4500
Dibenzofuran		8270D	0.0059	0.075	50	19-130	50	52-130	30	15	58
Hexachlorobutadiene		8270D	0.012	0.075	50	18-109	50	35-102	30	3.9	6.2
N-Nitrosodiphenylamine		8270D	0.0137	0.1	50	20-133	50	36-129	30	11	11
Ionizable Organic Compounds			ug/kg dry wt							ug/kg dry wt	
Phenol	ARI	8270D	14	100	50		50		30	420	1,200
2-Methylphenol		8270D	7.7	100	50	5-115	50	22-86	30	63	63
4-Methylphenol		8270D	22	100	50	5-143	50	48-123	30	670	670
2,4-Dimethylphenol		8270D	4.4	100	50	5-137	50	30-112	30	29	29
Pentachlorophenol		8270D	12	100	50	5-175	50	5-189	30	360	690
Benzyl Alcohol		8270D	15	100	50	5-135	50	5-73	30	57	73
Benzoic Acid		8270D	10	100	50	5-156	50	42-129	30	650	650
Polychlorinated Biphenyls			mg/kg dry wt							mg/kg OC	
Total PCB Aroclors[5]	Libby	8082	0.06	0.1	20	75-125	20	75-125	20	12	65
Dioxins and Furans			ng/kg dry wt								
2,3,7,8-TCDF	ARI	8290	0.244	1.0	25	--	--	75 - 158	25	--	--
2,3,7,8-TCDD		8290	0.214	1.0	25	--	--	67 - 158	25	--	--
1,2,3,7,8-PeCDF		8290	0.472	1.0	25	--	--	80 - 134	25	--	--
2,3,4,7,8-PeCDF		8290	0.625	1.0	25	--	--	68 - 160	25	--	--
1,2,3,7,8-PeCDD		8290	0.59	1.0	25	--	--	70 - 142	25	--	--
1,2,3,4,7,8-HxCDF		8290	0.784	1.0	25	--	--	72 - 134	25	--	--
1,2,3,6,7,8-HxCDF		8290	0.623	1.0	25	--	--	84 - 130	25	--	--
2,3,4,6,7,8-HxCDF		8290	0.574	1.0	25	--	--	70- 156	25	--	--
1,2,3,7,8,9-HxCDF		8290	0.953	1.0	25	--	--	78 - 130	25	--	--
1,2,3,4,7,8-HxCDD		8290	0.479	1.0	25	--	--	70- 164	25	--	--
1,2,3,6,7,8-HxCDD		8290	0.702	1.0	25	--	--	76 - 134	25	--	--
1,2,3,7,8,9-HxCDD		8290	0.722	1.0	25	--	--	64 - 162	25	--	--
1,2,3,4,6,7,8-HpCDF		8290	0.881	1.0	25	--	--	82 - 122	25	--	--
1,2,3,4,7,8,9-HpCDF		8290	0.703	1.0	25	--	--	78 - 138	25	--	--
1,2,3,4,6,7,8-HpCDD		8290	1.14	2.5	25	--	--	70- 140	25	--	--
OCDF		8290	1.77	2.0	25	--	--	63 - 170	25	--	--
OCDD		8290	9.42	10	25	--	--	78 - 144	25	--	--

Table 1: Chemical Parameters, Laboratory QC Limits, and SMS Criteria

Parameter	Laboratory	Analysis Method	MDL	RL	Duplicate RPD	Matrix Spike		Blank Spike/ LCS		Ecology Sediment Management Standards[1]	
						%R	RPD	%R	RPD	SQS	SIZmax
Total TCDF	ARI	8290	--	1.0	--	--	--	--	--	--	--
Total TCDD		8290	--	1.0	--	--	--	--	--	--	--
Total PeCDF		8290	--	1.0	--	--	--	--	--	--	--
TotalPeCDD		8290	--	1.0	--	--	--	--	--	--	--
TotalHxCDF		8290	--	1.0	--	--	--	--	--	--	--
TotalHxCDD		8290	--	1.0	--	--	--	--	--	--	--
TotalHpCDF		8290	--	1.0	--	--	--	--	--	--	--
TotalHpCDD		8290	--	1.0						--	--

Notes:

dry wt: dry weight, mg/kg: milligrams per kilogram, ng/kg: nanograms per kilogram, PSEP: Puget Sound Estuary Protocol, ug/kg: micrograms per kilogram.

mg/kg OC: milligrams per kilogram organic carbon normalized. The listed chemical parameter criteria represent concentrations in parts per million normalized or expressed on a total organic carbon basis. To normalize to total organic carbon, the dry weight concentration for each parameter is divided by the decimal fraction representing the percent total organic carbon content of the sediment.

[1]SMS criteria for the SQS and the SIZmax (WAC 173-204).

[2]The LPAH criterion represents the sum of the following low molecular weight polynuclear aromatic hydrocarbon compounds: Naphthalene, Acenaphthylene, Acenaphthene, Fluorene, Phenanthrene, and Anthracene. The LPAH criterion is not the sum of the criteria values for the individual LPAH compounds as listed.

[3]The HPAH criterion represents the sum of the following high molecular weight polynuclear aromatic hydrocarbon compounds: Fluoranthene, Pyrene, Benz(a)anthracene, Chrysene, Total Benzofluoranthenes, Benzo(a)pyrene, Indeno(1,2,3,-c,d)pyrene, Dibenzo(a,h)anthracene, and Benzo(g,h,i)perylene. The HPAH criterion is not the sum of the criteria values for the individual HPAH compounds as listed.

Table 2: Sediment Sample Analysis Summary, Preservation, Sample Container, and Holding Times

Analytical Parameter	Analysis Method	Sample Preservation	Technical Holding Time	Sample Container(s)
Total Solids	PSEP	Cool to 4°C	14 days from collection	One 8 oz wide mouth glass jar with teflon-lined lid
Total Volatile Solids				
Total Organic Carbon	9060	Cool to 4°C	14 days from collection	One 8 oz wide mouth glass jar with teflon-lined lid
		Freeze to -18°C	6 months from collection	
Grain Size	PSEP	Cool to 4°C	180 days from collection	One 16 oz wide mouth glass jar with teflon-lined lid
Total Sulfides	9030/PSEP	Cool to 4°C and preserve with 5mL zinc acetate	7 days from collection	One 2 oz wide mouth glass jar with teflon-lined lid
Ammonia	PSEP/Plumb	Cool to 4°C	7 days from collection	One 8 oz wide mouth glass jar with teflon-lined lid
SVOCs	8270D	Cool to 4°C	Extract within 14 days of collection; analyze within 40 days of extraction	One 8 oz wide mouth glass jar with teflon-lined lid
		Freeze to -18°C	Extract within 1 year of collection; analyze within 40 days of extraction	
PCBs	8082	Cool to 4°C	Extract within 14 days of collection; analyze within 40 days of extraction	One 8 oz wide mouth glass jar with teflon-lined lid
		Freeze to -18°C	Extract within 1 year of collection; analyze within 40 days of extraction	
Metals	6020/7471	Cool to 4°C	180 days (28 days for mercury)	One 8 oz wide mouth glass jar with teflon-lined lid
		Freeze to -18°C	2 years (28 days for mercury)	
Dioxins/Furans	8290	Cool to 4°C	Extract within 30 days of collection; analyze within 45 days of extraction	One 8 oz wide mouth glass jar with teflon-lined lid

Notes:

°C: degrees Celcius, PSEP: Puget Sound Estuary Protocol.

Attachment 1

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Standard Operating Procedure

Particle Size Distribution by Sieve Pipette PSEP Method

SOP 1115
Revision 000

Revision Date: 3/01/15
Effective Date: 3/01/15

Prepared By:

Beth Goble

Approvals:

Elizabeth Goble

Laboratory / Section Manager

Quality Assurance

Annual Review

SOP Number:	1115
Title:	Particle Size Distribution by Sieve Pipette – PSEP Method
Revision:	000
Revision Date:	3/01/15
Effective date:	3/01/15

The MTC employee named below certifies that this SOP is accurate, complete and requires no revisions.

Reviewer's Name	Reviewer's Signature	Date
Beth Goble	~~2-29-16~~	2-29-16
Beth Goble		3/1/17
Beth Goble		2/28/18
Beth Goble		3/1/19
BETH GOBLE		03-02-2020

1.0 PURPOSE AND SCOPE

This procedure describes methods, materials, equipment, and special conditions required to determine the particle size distribution for sediment samples by the PSEP Method. Wet sieving separates sample into two size fractions; particle sizes >#230 sieve, and particle sizes <#230 sieve. Fine fractions are further subdivided using a pipette technique that depends on the differential settling rates of different sized particles.

Particle size determinations can either include or exclude organic material. If organic material is removed prior to analysis, the "true" (i.e., primarily inorganic) particle size distribution is determined. If the organic material is included in the analysis, the "apparent" (i.e., organic plus inorganic particle size distribution is determined).

2.0 EQUIPMENT

2.1 BALANCE - Capable of precision to 0.1mg
2.2 DRYING OVEN – A thermostatically controlled chamber capable of maintaining a uniform and consistent temperature of 90 ± 2° C.
2.3 MECHANICAL SIEVE SHAKER – A mechanical device used to shake and vibrate a nest (stack) of sieves at a constant rate and energy level to separate a given sample into the individual particle sizes.
2.4 SIEVES – A nest of sieves including #4 (4.75mm), #10 (2.0mm), #18 (1.0mm), #35 (500μm), #60 (250μm), #120 (125μm) and #230 (62.5μm).
2.5 TIMER – A suitable timing device capable of measurements to the nearest second
2.6 SEDIMENTATION CYLINDERS
2.7 RUBBER STOPPER – A No. 13 stopper to fit in the sedimentation cylinders
2.8 DESICCATOR
2.9 25ml in 1/10 PIPETTE – With a rubber suction bulb
2.10 FUNNEL – Large enough to nest a #230 sieve in
2.11 RUBBER POLICEMAN
2.12 ALUMINUM TARE DISHES – Of a size to fit on the balance
2.13 BRISTLE BRUSHES
2.14 SIEVE BOARD – Tag Board, smooth and large enough to empty 8" diameter sieves on
2.15 LAB STAND – With clamps
2.16 LABEL TAPE
2.17 SPOONS
2.18 MIXING BOWL – For sample homogenization

3.0 REAGENTS

3.1 10% HYDROGEN PEROXIDE (OPTIONAL) – To make 100ml 10% Hydrogen peroxide solution dilute 33.3mls of 30% hydrogen peroxide to 100ml.
3.2 Solution of SODIUM HEXAMETAPHOSPHATE $Na(PO_2)_6$ – A solution is made by mixing 40 grams sodium hexametaphosphate $Na(PO_2)_6$ in 1000ml of distilled water (0.1 Molar). Mix the solution thoroughly and let stand overnight. Pipette 5, 10 ml aliquots into weighed tares and oven dry. Record the dry weight in the batch notebook. Average the five weights and record average in notebook. The solution expires in one month.

4.0 DEFINITIONS

4.1 *Test Environment* – A fairly constant temperature of approximately 20° C during analysis. Small fluctuations in temperature may introduce differences that are of practical significance.
4.2 *Sieve Time* – Samples will be sieved for 12 minutes.
4.3 *Sieves* – Sieves are frames that hold wire cloth that has various size openings. The operator will visually examine the sieves for defects (i.e., tears, plugging, holes) prior to each use. Do not use damaged sieves.
4.4 *Flocculation* – The process where finely suspended particles agglomerate and settle out of solution

5.0 DOCUMENTATION

5.1 PIPETTE GRAIN SIZE ANALYSIS data sheet 1115F.

6.0 PROCEDURE

6.1 Sample Preparation
6.1.1 Remove the samples from the cooler/refrigerator and allow them to warm to room temperature. Check the MTC sample numbers against the client numbers to verify that they are correct. Notify supervisor for ID discrepancies.
6.1.2 If requested by the client, remove organic material from the sample according to section 6.2.
6.1.3 Label and pre-weigh two tare dishes, one for the moisture content portion of the sample and one for the wet sieving portion.
6.1.4 Carefully homogenize the sample to incorporate any overlying water.
6.1.5 Remove the total solids portion of the sample (approximately 25 grams), weigh it in the labeled tare dish, and record the mass on the data sheet to the nearest 0.1mg. Dry the sample in oven overnight or until completely dry, cool it in a desiccator, weigh, and record the mass on the data sheet.
6.1.6 Split the test portion of sample (approximately 40 to 150 grams), weigh it in the appropriate tare dish, and record the mass on the data sheet to the nearest 0.1mg. The critical factor for the sample size determination is the weight of the fine-grained material that will be used for the pipette analysis. Ideally, the total dry weight of fine-grained material in the sedimentation cylinder should equal approximately 15 grams, and the acceptable range is between 5 and 25 grams. Estimate the fraction of material finer than the #230 sieve, along with the moisture content (i.e., if the moisture content is 100%, and the percent finer than the #230 is estimated at 50%, an acceptable sample size could be approximately 80 grams).
6.1.7 Clean workstation when sample preparation is finished. Initial and date data sheet.

6.2 Organics Oxidation (optional)
6.2.1 Place sample in large beaker (≥2000ml)
6.2.2 Add 20 ml of 10% hydrogen peroxide solution and mix thoroughly.
6.2.3 Let sample stand until frothing stops.
6.2.4 Add an additional 10ml of 10% hydrogen peroxide solution and mix. Continue adding 10ml portions of solution until no frothing occurs.
6.2.5 Gently boil sample on hotplate to remove excess hydrogen peroxide. Be careful not to lose any material during boiling operation. See section 9.0 CORRECTIVE ACTION if a significant amount of material is lost during boiling operation.

6.3 Wet Sieving
6.3.1 Label sedimentation cylinders with the MTC sample ID using label tape.

6.3.2 Place a #230 sieve in the funnel over a sedimentation cylinder using lab stands with clamps. Moisten the sieve mesh using a light spray of distilled water.
6.3.3 Add 20-30mls of distilled water in sample tare dish and stir to suspend the fine-grained material.
6.3.4 Decant the liquid onto sieve and gently agitate sieve to separate fractions. Aggregated clumps of sediment can be gently broken down with a rubber policeman. For sample spillage, see 9.0 CORRECTIVE ACTION.
6.3.5 Continue washing sample with a fine spray of distilled water and decanting the supernatant until only clear water passes through sieve. See 9.0 CORRECTIVE ACTION if liquid passes 1000ml mark.
6.3.6 Rinse all remaining material off the #230 sieve back into the tare dish. Place sample in the oven overnight or until dry (usually 8-16 hours).
6.3.7 Clean the workstation when wet sieving is finished. Initial and date the data sheet.

6.4 Sieving the Sand-Gravel Fraction
6.4.1 Once dry, remove washed plus #230 material dish from the oven and put into the desiccator to come to thermal equilibrium.
6.4.2 Set up a nest of sieves with the coarsest on the top and grading down to the finest on the bottom over a sieve pan. This set of sieves will include the #4, #10, #18, #35, #60, #120, and #230. Clean any dirty sieves with a wire or bristle brush and tap each sieve on the table with all edges evenly to remove debris.
6.4.3 Weigh the sample and tare dish and record the mass on the data sheet to the nearest 0.1mg.
6.4.4 Add the sample to the uppermost (#4) sieve in nest. Use a brush to clean the entire sample from the tare dish and gently break up any agglomerations of material that may have formed due to drying.
6.4.5 Place the nest of sieves in the mechanical sieve shaker and place the metal lid with cork right side up on the top of the stack. Set shaker arm in the down position, set timer for 12 minutes, and start the shaker. Close the sound enclosure lid and start the exhaust fan. Remove the nest of sieves when shaker is finished.
6.4.6 Empty the top sieve by inverting it over the glossy tag board. Run a bristle brush over the entire sieve mesh to remove all particles. Tap sieve evenly on table.
6.4.7 Carefully pour sample from the tag board into the tare dish, weigh the fraction to the nearest 0.1mg, and record the mass on the data sheet.
6.4.8 Repeat 6.4.6 and 6.4.7 with each remaining sieve. Each mass recorded on the data sheet will be a cumulative mass. Tare out the weight of an empty foil tan on the balance and pour the contents of the sieve pan into it. Weigh and record the mass of the < #230 material on the data sheet. Empty the contents of the foil pan into the silt-clay fraction in the sedimentation cylinder. Compare the total weight retained with the original dry weight to ensure that no material was lost in the sieving process. If weights are significantly different, see section 9.0 CORRECTIVE ACTION. Note large amounts of organic material (e.g., wood debris, grass, shells) or unusual material in any size fraction on the data sheet.
6.4.9 Clean workstation when work is finished. Initial and date the data sheet.

6.5 Pipetting the Silt-Clay Fraction
6.5.1 Add 10ml of $Na(PO_2)_6$ dispersant to each silt-clay fraction cylinder and fill to the line with distilled water. Record the batch number of dispersant used on data sheet.
6.5.2 Using a No.13 rubber stopper, mix suspensions by inverting cylinder end over end for 60 cycles.
6.5.3 Allow the mixed suspension to stand for 2-3 hours and check for signs of flocculation. See 9.0 CORRECTIVE ACTION if flocculation occurs.

6.5.4 Label and pre-weigh seven fraction tares to the nearest 0.1mg and record the mass on the data sheet.
6.5.5 Print out a set of withdrawal time stickers on the computer. Attach the stickers to the corresponding data sheets.
6.5.6 Use the rubber stopper and mix suspensions by inverting cylinder end over end approximately 60 times per one minute. For sample spillage see 9.0 CORRECTIVE ACTION.
6.5.7 Within 20 seconds, withdraw a 20ml aliquot from a depth of 20cm below the surface of the suspension using a 25ml 1/10 pipette with rubber bulb. It is critical that the solution be disturbed as little as possible when the pipette aliquots are taken.
6.5.8 Transfer aliquot to the corresponding pre-weighed tare and rinse pipette by drawing approximately 20ml distilled water into pipette and transferring rinse into the same tare.
6.5.9 Withdraw another 20ml aliquot at the depth of 10cm below the surface of the suspension at the appropriate time as listed in TABLE 1 according to room temperature. For missed pipetting times see 9.0 CORRECTIVE ACTION.
6.5.10 Dry all aliquots in oven to a constant weight at 90°C.
6.5.11 Cool dried samples to room temperature in a desiccator, weigh to the nearest 0.1mg, and record on data sheet.
6.5.12 Keep workstation clean. Initial and date data sheet.

TABLE 1. Withdrawal Times for Pipette Samples

Diameter Finer (phi)	Diameter Finer (um)	Withdrawal Depth (cm)	Elapsed Time for Withdrawal of Sample in Hours (h) Minutes (m) and Seconds (s)						
			18°	19°	20°	21°	22°	23°	24°
4.0	62.5	20	20s	20s	20s	20s	20s	20s	20s
5.0	31.2	10	2m	1m 57s	1m 54s	1m 51s	1m 49s	1m 46s	1m 44s
6.0	15.6	10	8m	7m 48s	7m 36s	7m 25s	7m 15s	7m 5s	6m 55s
7.0	7.8	10	31m 9s	31m 11s	30m 26s	29m 41s	28m 59s	28 m 18s	27 m 39s
8.0	3.9	10	2h 8m	2h 5m	2h 2m	1h 59m	1h 56m	1h 53 m	1h 51 m
9.0	1.95	10	8h 32m	8h 18m	8h 6m	7h 56m	7h 44m	7h 32 m	7h 22 m
10.0	0.98	10	34h 6m	33h 16m	32h 28m	31h 40m	30h 56m	30h 12 m	29h 30 m

6.6 SALT CORRECTIONS – Optional – By Client Request
6.6.1 After all the pipette aliquots have been taken pipette approximately 40ml of sample into a plastic test tube labeled with the appropriate sample ID.
6.6.2 Place the test tubes from each sample into an appropriate centrifuge holder, arranging the test tubes to be balanced around the center of the holder. Distribute the test tubes so each holder has the same number. Use a test tube filled with DI water in the center of the holder to balance all four holders to within 0.1g.

6.6.3 Place the four balanced test tube holders in the centrifuge, close the lid and spin the tubes for 15 minutes at 2500 x g.
6.6.4 Set up vacuum apparatus with vacuum flask, filter frit and cup.
6.6.5 Use tweezers to place a 0.45µm filter on the frit. Do not touch the filter with hands.
6.6.6 Pipette at least a 30ml aliquot from the centrifuge tube into the filter cup and turn the vacuum on.
6.6.7 When all the liquid has passed through the filter, turn off the vacuum and remove filter cup from flask. Pipette exactly 20ml of filtered liquid from the vacuum flask into a pre-labeled, pre-weighed tare. Rinse the pipette with an aliquot of DI water into the sample tare. Place tare in a drying oven set at 90°C $\pm$ 5°.
6.6.8 Dispose of the filter. Rinse the filter flask, and cup with DI water and allow the equipment to dry.
6.6.9 Repeat steps 6.6.1 through 6.6.8 for each sample. Be sure equipment is dry before beginning the next sample.
6.6.10 When samples are dry, remove the tares from the oven and place them in a desiccator. Once the samples have reached thermal equilibrium, remove the tares from the desiccator and weigh immediately on the analytical balance.
6.6.11 Multiply the dry weight of the sample (minus the tare weight) by 50 to calculate the weight of salt in the 1000ml sample.

6.7 Data Entry – Open the appropriate Excel Template file and enter the data from the bench sheets into the labeled data cells. Excel will perform the calculations.

7.0 CALCULATIONS

7.1 MOISTURE CONTENT and TOTAL SOLIDS

Total solids content is determined as follows:

$$\text{Percent Solids} = \frac{(A - B)(100)}{(C - B)}$$

Where: A = weight of tare and dry sample residue
B = weight of tare
C = weight of tare and wet sample

7.2 SAND and GRAVEL FRACTION

The sand and gravel fractions of the sample are reduced as follows:

$$\text{Percent retained (for a given sieve)} = C/D * 100$$

Where: C = cumulative mass retained for a given sieve
D = total dry sample mass

7.3 SILT and CLAY FRACTION

The total mass of the phi-sized interval in the 1000ml graduated cylinder is determined as follows:

$$\text{Phi mass} = 50((E - G) - (F - G))$$

Where: E = mass of residue in a 20ml aliquot for a given phi size boundary
F = mass of residue in a 20ml aliquot for next larger

phi size boundary
G = mass of dispersant and dissolved salt in a 20ml aliquot

8.0 SAFETY

8.1 Gloves should be worn at all times. Lab wear including a lab coat and safety glasses are provided. Care should be taken not to inhale fine dust while sieving. A dust mask should be worn when sieving.
8.2 The sieve shaker is loud, and the lid should be closed while in operation.
8.3 Keep workstation clean at all times. Wipe any spills to avoid safety hazards.

9.0 CORRECTIVE ACTION

9.1 When sample is lost during the oxidation of organic matter, notify the laboratory supervisor. A significant loss of sample may require re-analysis.
9.2 Sample loss during wet sieving - If sample is spilled on table, use distilled water to wash spillage into tare dish. If sample is lost on the floor, see supervisor. A significant loss may result in a re-analysis.
9.3 Excess wash volume – If wash volume exceeds 1000ml mark during wet sieving, let sample evaporate to obtain an acceptable volume.
9.4 Sample loss during sieving – Attempt to brush spilled sample into tare dish prior to weighing. It is extremely important to keep worktables and floor clean prior to sieving in case a spill occurs.
9.5 Sample Flocculation – Flocculation results in a curdling and rapid settling of lumps of particles or by the presence of a thick, soupy layer on the bottom of the cylinder passing abruptly into clear water above. When flocculation occurs, add dispersant in 10ml increments until no noticeable flocculation is observed. Record the total volume of dispersant added on the data sheet.
9.6 Sample spillage during cylinder mixing – If rubber stopper is not tight on cylinder and spillage occurs, continue pipetting procedure. Note approximate amount of spilled liquid and note on data sheet.
9.7 Missed pipetting aliquots – If withdrawal is missed the suspension may be re-mixed and the missed aliquot can be taken at the appropriate time. It is not necessary to take the initial 20ml aliquot for this corrective action.
9.8 The quality assurance (QA) ratio range is between 95% and 105%. If the sample is outside of the allowable range, the sample must be rerun. If the sample cannot be rerun, a data qualifier must be assigned to the sample to explain why the sample is out of range.

10.0 REFERENCES

10.1 Folk, Robert L., 1978, The Petrology of Sedimentary Rocks, Hemophile Publishing Co., Austin TX

10.2 USACE 1995, Puget Sound Estuary Protocols, U.S. Army Corps of Engineers, Seattle WA

Analytical Resources, Incorporated
Analytical Chemists and Consultants

Standard Operating Procedure

Sulfide Preservation and Distillation

SOP 640S
Revision 006

Revision Date: 11/30/16
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Prepared by:

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Eric Larson, Inorganics Division Manager

Annual Review

SOP Number:	640S
Title:	Sulfide Preservation and Distillation

The ARI employee named below certifies that this SOP is accurate, complete and requires no revisions

Name	Reviewer's Signature	Date

STANDARD OPERATING PROCEDURES Sulfide Preservation and Distillation

1. Scope and Application

1.1. Sulfide in environmental samples may exists in a variety of states dependent upon pH and redox potential of the sample matrix. Primary forms include H_2S, HS^-, S^{-2}, and various metal sulfide complexes that vary widely in their degree of solubility.

1.2. This SOP describes the procedures used by ARI to preserve sulfide contained in environmental samples and to release the combined sulfides into a form (H_2S) that is measurable by routine finish analyses. The finish analyses, iodometric titration and methylene blue colorimetry, are covered under separate SOPs, ARI 650S and 653S, respectively.

1.3. This SOP is written to conform with the requirements of: Standard Methods 4500-S^{2-} Sulfide; Plumb, 1981; USEPA and Puget Sound Water Quality Authority PSEP) 1986; SW-846 Method 9030B (Acid Soluble only); and, Allen, et al. 1991 (Acid Volatile Sulfides and Simultaneously Extractable Metals).

2. Summary of Procedure

2.1. There are multiple procedures available. The client, and Project Manager must select the appropriate procedure for their needs prior to sampling and receipt of samples by the laboratory.

2.2. Aqueous samples can be analyzed for:

2.2.1. Dissolved sulfide if the sample is:

2.2.1.1. Unpreserved and contains no particulates.

2.2.1.2. Unpreserved and contains particulates that are removed by flocculation prior to finish analysis.

2.2.2. "Total sulfide"

2.2.2.1. Without distillation if the sample has been preserved with zinc acetate and is sufficiently clear (without significant turbidity) to allow either titrimetric or colorimetric analysis; or

2.2.2.2. With distillation if the sample has been preserved, is turbid, and cannot be read directly (*note: SW-846 Method 9030B is the only distillation procedure that covers aqueous samples*)

2.3. Sediment / soil or highly turbid aqueous samples are acidified under anoxic conditions to release sulfide from the matrix as H_2S. The released H_2S gas is then trapped in zinc acetate solution to precipitate sulfide (as zinc sulfide). Finish analysis is conducted on the trapping solution. **Three distillation procedures are available: SW-846 Method 9030B (Acid Soluble), PSEP 1986, and Acid Volatile Sulfide (AVS).** These vary primarily in the pH and temperature conditions under which the distillation is conducted and do not necessarily release equivalent amounts of sulfide as noted in Sections 3.7 and 3.8 below.

2.4. Sulfide can form highly insoluble complexes with a number of metals that might not be released for analytical determination by the procedures employed here. In this sense, “Total sulfide” actually represents that amount of sulfide that is released under the conditions of the distillation and not, necessarily, the total amount of sulfide that is present in the sample matrix.

3. Definitions

3.1. Sulfide: Sulfide exists in a variety of states dependent upon pH and redox potential of the sample matrix. Forms include hydrogen sulfide (H_2S), bisulfide ion (HS^{-1}), sulfide ion (S^{-2}), and metal sulfide complexes which vary widely in their degree of solubility (generally pH dependent dissociation to bisulfide and metal ions). Dissolved hydrogen sulfide (H_2S) and bisulfide ion (HS^{-1}) exist in equilibrium dependent upon pH and ionic strength with gaseous H_2S predominating at low pH. Sulfide ion (S^{-2}) is usually negligible due to the high dissociation constant for bisulfide to sulfide.

3.2. Hydrogen Sulfide. Combines with metals to form slightly soluble metal precipitates. Normally, these will respond to the acidic conditions used in the finish analyses to release the “acid soluble” sulfide into a measurable form (H_2S). Some metal complexes are virtually insoluble (copper and silver sulfides), will not respond to the test conditions and thus are not included in the definition of either Total or Dissolved Sulfide.

3.3. Hydrogen Sulfide Gas. Toxic to humans, creates nuisance odors, and can lead to serious corrosion problems. Dissolved hydrogen sulfide is toxic to aquatic organisms and partitioning into H_2S and HS^{-1} is sometimes required to more closely define possible toxicity.

3.4. Acid Volatile Sulfide. The presence of various iron sulfides (mackinawite, Fe(II) monosulfide, greigite, Fe_3S_4 and some pyrite, FeS_2) and the development of slightly soluble metal sulfide precipitates in anoxic sediments and sludge’s leads to the formation of a class of sulfides referred to as Acid Volatile Sulfides (AVS). These are operationally defined by the conditions of extractive distillation. Our AVS procedure follows Allen, et al. (1991). AVS are significant since they are thought to influence the bioavailability of toxic metals in sediments. Simultaneously Extracted Metals (SEM) in the digest solution are often determined to address the relationship between metals and sulfide in the sample being tested. Acid Volatile Sulfide (AVS) is defined as solid phase sediment sulfide which is released by extraction in hydrochloric acid (1 to 1.2 N HCl) at room temperature for 60 minutes. Evolved H_2S is trapped in Zinc Acetate solution. The procedure described here for the extraction of AVS follows Allen, et al. 1991 (EPA Draft Method 1991).

3.5. Dissolved (Soluble) Sulfide. Includes aqueous phase sulfide which remains in solution after suspended solids have been removed by flocculation and settling with aluminum chloride and sodium hydroxide. Dissolved sulfide can only be determined on samples which have not been preserved with zinc acetate.

3.6. "Total sulfide." Includes dissolved soluble sulfides as well as most metal complexed sulfides with the exception of some highly insoluble forms (e.g. CuS, AgS, SnS_2). The analysis of total sulfide in solid phase samples (soils or sediments) is operationally defined by the procedure used to extract the sulfide from the sample matrix. Extraction is conducted by acid distillation from the sample matrix, the main difference between the distillation procedures is the acid used for extraction, the pH of the extracting medium and temperature. Different conditions of distillation can lead to significant variations in the amount of sulfide released when different procedures are used on the same sample. PSEP is the least aggressive of the distillation protocol (pH 3 to 4) and should be expected to release the least amount of sulfide from the matrix. Method 9030B is more rigorous (pH <1) and should provide a better estimate of the total acid soluble sulfide. AVS uses a 1 to 1.2 N HCl extracting solution with a theoretical pH of 0 and should be the most acidic and aggressive of the distillation procedures.

3.7. Puget Sound Water Quality Authority 1986 (PSEP) "Total Sulfide". This is the acidification of a sediment sample with pre-treated, concentrated hydrochloric acid to methyl orange pH (3.5 - 4.5) with heated distillation (90ºC). Our procedure is a modification of the original PSEP method using a bromophenol blue indicator (pH 3.0 - 4.6) and temperatures below the boiling point to avoid carry over of water into the zinc acetate trapping solution. There is no specified time period for extraction but 60 minutes would be consistent with other extraction procedures.

3.8. EPA SW-846 Acid Method 9030B (Acid Soluble Sulfide). This procedure estimates total acid soluble sulfide as that sulfide released by sulfuric acid extraction at 70 ºC and a pH <1 for 90 minutes. It does not include the highly insoluble metal complexes. Trapping is conducted in zinc acetate with formaldehyde added to prevent interference associated with other reduced forms of sulfur. Iodometric titration is the prescribed finish analysis. The ARI procedure is modified to use a colorimetric finish analysis hence removing the requirement for using formaldehyde in the trapping solution.

3.9. Preparation and Analytical batches. Environmental samples that are prepared and/or analyzed together with the same process and personnel, using the same lot(s) of reagents.

3.9.1. Preparation batch: Involves a sulfide distillation and is composed of one to twenty environmental samples of the same quality systems matrix, meeting the above mentioned criteria and with a maximum time between the start of processing of the first and last sample in the batch to be 24 hours. The twenty environmental samples do not include method blanks, LCS, matrix spikes or matrix duplicates. At a minimum, each batch must include a Method Blank, a Laboratory Control Standard, and a Detection and Quantitation Limit (DQL) standard prepared at a concentration equal to the low curve point (0.05 mg/L) for colorimetric finish and/or the reporting limit (1 mg/L) for titrimetric analysis.

3.9.2. Analytical batch: (i.e. just the colorimetric analysis or the titrimetric analysis) is composed of prepared environmental samples (extracts, digestates or concentrates) which are analyzed together as a group. An analytical batch can include prepared samples originating from various quality system matrices and can exceed 20 samples (NELAC 2007. Quality Systems: General Requirements. The NELAC Institute, V1M2 CLN_IS_122807, December, 2007).

4. Interferences

4.1. Sulfide is highly volatile and subject to rapid oxidation to elemental sulfur and sulfate. Exercise care in the handling of samples to minimize atmospheric contact during all phases of the sub-sampling and distillation procedures.

4.2. Aqueous samples preserved with zinc acetate/sodium hydroxide will have the sulfide bound in a zinc sulfide precipitate. This precipitate must be uniformly distributed throughout the sample bottle by <u>gentle</u> mixing prior to withdrawing the aliquot for analysis.

4.3. Volatilization (even under anoxic conditions) can be particularly problematic for solid phase samples where sulfide is typically not uniformly distributed within the sample matrix and sample jar. Try to mix the sample rapidly and within the original sample jar. Highly variable replicate results and matrix spike recoveries can result. Note any unusual characteristics in the appearance or smell of the sample (layers of different color, particularly black or red). Loss of volatile sulfide will be immediately evident by the characteristic "rotten egg" smell and should be noted as a potential negative bias in the observed result.

4.4. Highly calcareous sediments or soils (e.g. marine sediments containing shell fragments) will tend to neutralize the acid over the course of the distillation. This is particularly a problem for AVS determination where there is no control or compensation for potential acid neutralization. PSEP distillation uses a pH color indicator to adjust acid addition and 9030B requires pre-determination of the required acid volume. AVS calls only for the addition of a set amount of 6N hydrochloric acid to achieve the final normality of 1.0 to1.2 (pH 0). 20 mL acid is added to 100 -120 mL of sediment-water matrix (including the water content of the sediment).

5. Safety

5.1. The toxicity or carcinogenicity of each reagent used in this SOP has not been precisely defined. Treat each chemical compound as a potential health hazard. Reduce exposure to all chemicals to the lowest possible level by whatever means available.

5.2. Hydrogen sulfide gas is toxic to humans and creates nuisance odors. Sediment extraction must be conducted in a fume hood.

5.3. Always wear appropriate PPE (personal protective equipment) when working in the Laboratory. Gloves, safety glasses, ear protection, lab coats, respirators, face shields, and other safety items are provided for your protection.

5.4. Environmental Samples may contain hazardous waste; treat them as potential health hazards.

5.5. All sample waste must be disposed following the ARI Waste Management Plan.

5.6. Dispose of all unwanted, broken glassware into a broken glassware disposal box. Inspect every piece of glassware. Do not use any that are chipped, cracked, etched, or scratched. Glassware with minor damage should be stored for repair.

6. Equipment and Supplies

6.1. Gas Evolution Apparatus (see Figure below).

6.1.1. 250 mL, 3 neck distillation flasks, 24/40 ground glass joints (Kontes 606020-0624)

6.1.2. Nitrogen gas inlet adaptor, 24/40 taper (Kontes 179700-0824)

6.1.3. Outlet adaptor, 24/40 taper (Kontes 183000-2440)

6.1.4. Acid addition funnel, 125 mL, 24/40 taper (Kontes 634580-0125)

6.1.5. 125 mL gas washing bottles with straight glass frit (Wilmad LG-3761-100)

6.1.6. Teflon sleeves for 24/40 ground glass joints (Fisher 14-320 F)

6.1.7. Optional: Keck clips for 24/40 joints (Fisher CG14505) of each distillation unit.

6.2. 6-place stirring / heating manifold for 250 mL flasks (Electrothermal, EME Series Electromantle). The control knob set points on each mantle giving temperatures of 70 and 90 °C in the reaction flask should be determined and marked for use in future distillations.

6.3. Nitrogen gas cylinder with nitrogen regulator (10 psi maximum pressure).

6.4. Oxygen trap for nitrogen supply (Altech Oxy-Trap AT4001 coupled with Indicating Oxy-Trap AT4004).

6.5. pH meter and electrode

6.6. Top loading balance (accurate to 0.001 gram)

6.7. Environmental Express Vessels, 100 ml plastic graduated tubes with white screw cap.

6.8. Weighing Paper, 3” x 3”. Fisherbrand Cat. No. 09-898-12A.

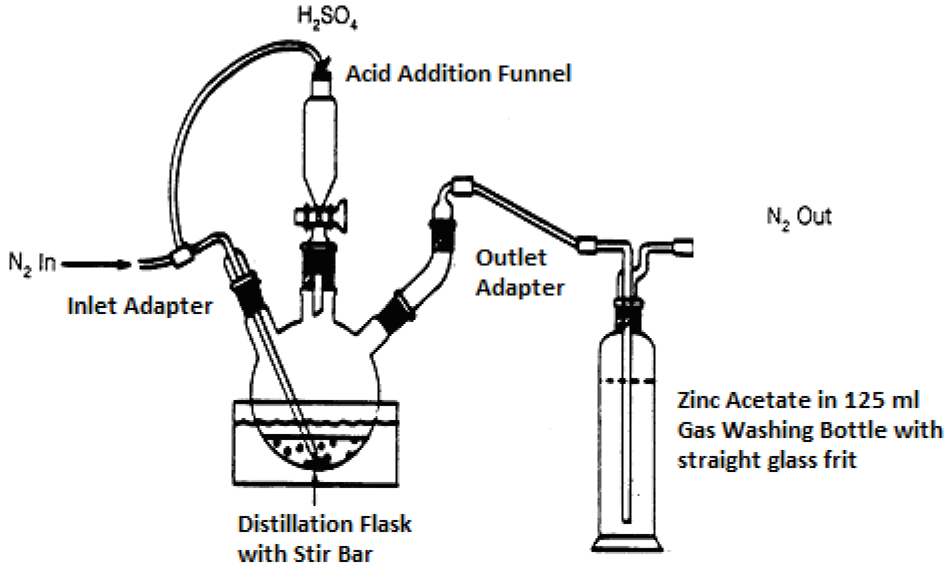

Figure. General setup for a Sulfide Distillation.

7. Reagents

7.1. Deoxygenated Reagent Water. Some reagents and all sample dilutions should be made with deoxygenated / deionized water (DDIW). A sufficient volume (enough to last for the days use) should be prepared daily by purging with an inert gas (e.g. helium or nitrogen) for at least 20 minutes. Keep the container tightly closed and open only when needed. This nitrogen purged water will also be used as a dispersing medium for distillation, as required.

7.2. Zinc acetate for preservation (2N = 1M): Dissolve 220 g Zinc acetate ($Zn(C_2H_3O_2)_2 \bullet 2H_2O$, FW = 219.49) in 800 mL DI and dilute to final volume of 1000 mL with DI. Store in polyethylene or glass bottle.

7.3. Zinc acetate trapping solution (0.2N = 0.1M): Add 5 ml of 6N NaOH and 20 ml of Acetic Acid to 200 ml of 2N Zinc Acetate solution and dilute to 2 liters.

7.4. Sodium Hydroxide (1 M = 1N): Dissolve 40 grams NaOH in DI water and dilute to 1 liter. Store in a polyethylene bottle.

7.5. PSEP Distillation Reagents.

7.5.1. Hydrochloric acid (HCl, treated): In a fume hood, carefully place one or two strips of aluminum foil in a beaker containing 250 mL concentrated HCL (vigorous reaction). After reaction, decant HCL to a separate bottle for use with PSEP distillations.

7.5.2. Zinc acetate trapping solution (Section 7.4)

7.6. 9030B Reagents

7.6.1. Sulfuric acid (H_2SO_4 concentrated): Use for adjusting distillation to pH ≤ 1 in 9030B distillation.

7.6.2. Zinc acetate trapping Solution (Section 7.4). Formaldehyde called for in the method is omitted because ARI use a colorimetric finish rather than the iodometic titration called for in the method.

7.7. AVS Reagents

7.7.1. Hydrochloric acid (6M): Carefully, and with mixing, add 500 mL conc. HCl to 400 mL DI then bring to a final volume of 1000 mL. Purge with nitrogen for 1 hour prior to use. <u>If used for AVS/SEM extraction, use ultrapure HCl. If only AVS, use our standard HCl.</u>

7.8. Aluminum chloride ($AlCl_3$•$6H_2O$, Fisher S75023): Aluminum chloride hexahydrate will rapidly accumulate water and become caked. Purchase in 100 gram bottles (Fisher S75023) and use the complete 100 grams each time a solution is prepared. Dissolve the contents of the bottle in 144 mL of reagent water.

7.9. Sodium hydroxide (NaOH, 6M): Dissolve 120 grams NaOH in 300 mL reagent water. CAUTION: NaOH solution will get hot! Cool and dilute to 500 mL. Store in a plastic bottle.

7.10. Sodium sulfide Standards: Sodium sulfide standards are required for batch and matrix quality control during distillation (LCS and matrix spikes). Sulfide standards cannot be accurately weighed. Prepared solutions must be standardized by iodometric titration before use. Instructions for doing this are contained in the Sulfide, Iodometric Titration SOP.

8. Sample Collection, Preservation, Shipment and Storage

8.1. Samples for "Total Sulfide" must be preserved at the time of collection. Unless the requested analysis is for soluble or dissolved sulfide, preservation of aqueous samples is accomplished in the field by the addition of zinc acetate resulting in the formation of slightly soluble zinc sulfide (a white colored precipitate). The pH of the sample must also be adjusted to greater than 9 with sodium hydroxide. Sample bottles sent out to clients will contain the required volume of 2N zinc acetate (2 mL of 2N /500 mL sample volume). To avoid the transport and usage of caustic chemicals by field personnel, sodium hydroxide is added once the samples are returned to the laboratory. Upon receipt in the laboratory, the samples are adjusted to pH >9 using 6N sodium hydroxide. The lab must verify that the sample bottle is labeled "zinc acetate" and that the pH is greater than 9. Laboratory personnel will add zinc acetate and sodium hydroxide as necessary.

8.2. Analysis should proceed as soon as possible after collection. The regulatory holding time for analysis is 7 days from the date of collection (EPA 2012, 40 CFR Part 136.3, Identification of Test Procedures, Table II). Standard Methods (SM1060 Table 1) allows a 28 day holding time for preserved samples while recognizing the regulatory holding time of 7 days.

8.3. Analysis for "Dissolved Sulfide" can only be conducted on samples which have not been preserved and should be run within 24 hours of collection.

8.4. Sediment samples can be collected in either glass or plastic jars. These can be preserved by addition of 2N zinc acetate over the surface (2 mL / 2 oz jar) but the efficiency of this treatment is unknown (Plumb, 1981). Sediment and waste samples should be transported to the lab on ice and stored at 4 ºC. Plumb, 1981 does not specify a holding time other than "as soon as possible". Standard Methods (4500-S2- A.3, Sampling and Storage) states that analysis should be conducted within 14 days. ARI standard procedure is to analyze within 7 days.

8.5. AVS samples should be filled with minimal head space and stored at 4 ºC. The maximum holding time for AVS sulfide is 14 days.

8.6. Solid samples require homogenization prior to sub-sampling the aliquot for analysis. Sulfide can rapidly volatilize during mixing hence the mixing should be done quickly and within the original sample container just prior to withdrawing the aliquot for analysis. Note any unusual characteristic or occurrence that could bias the sample result (e.g. if a sulfide odor is noted during the homogenization indicating that sulfide is being volatilized and the result will have a low bias). If possible, samples for Total Solids analysis should be taken after the aliquot for sulfide determination has been withdrawn.

8.7. All samples within a sulfide job should be analyzed the same way, either as preserved or unpreserved for each matrix set to not compromise data.

9. Quality Control *(Essential QC components following 40 CFR Part 136.7, May 18, 2012, EPA 2012 Method Update Rule).*

9.1. Demonstration of Capability. Each analyst performing this procedure must complete an initial "Demonstration of Capability" by preparing and analyzing 4 replicates of a QC Check Solution through distillation procedure. The recovery (Accuracy) must be within the range of ±10% with a relative standard deviation (Precision) less than 1%.

9.2. Method Detection Limit. The detection and quantitation limits for the methods are determined following the procedures described in ARI SOP 1018S

9.3. Laboratory Reagent Blank (Method Blank). Used as a Negative Control to verify the absence of contamination. Negative control is provided by a preparatory Method Blank. The preparatory Method Blank consists of DI water that has been processed along with and under the same conditions as associated samples. One Method Blank is processed along with each analytical batch of 20 samples. Ottawa sand should be used in conjunction with DI water for the solid phase method blank.

9.4. Laboratory Fortified Blank (Blank Spike or Laboratory Control Sample). Used as a Positive Control for the recovery of known additions. Positive control is provided by the analysis of a Laboratory Control Standard (LCS) which is equivalent to a laboratory fortified blank. The Laboratory Control Standards are processed exactly the same as the samples in the associated analytical batch. The LCS is spiked with sulfide solution which has been standardized by iodometric titration. This standard is used to verify recovery through all steps of the batch analysis.

9.5. Matrix Spike (MS) and Matrix Spike Duplicate (MSD). Matrix spikes will be run for each of 1 in 20 client samples (5% spiking) or as requested by the client. These spikes will be used to evaluate the accuracy (% Recovery) of the analysis relative to the sample matrix. Spiking will be at a level in the range of 1 to 10 times the sample background or at a minimum of 0.5 mg/L (10 times the low curve point). MSD's for the evaluation of the precision of the analysis (Relative Standard Deviation, RSD) will be run upon request of the client. Otherwise, precision of the analysis will be evaluated by the duplicate analyses.

9.6. Matrix Duplicates and Matrix Triplicates: Matrix duplicates will be run for each of 1 in 20 client samples (5%) or as requested by the client. Triplicates may be run at client request. These samples will be used to evaluate the variability of the sampling and analysis for a given sample matrix.

9.7. Internal Standards and Surrogate Standards are not applicable to colorimetric sulfide analysis.

9.8. Control charts for trend analysis. Control charts for the analysis of the Method Blank and LCS will be constructed and updated monitor method performance.

9.9. QC samples will be run with each batch of samples as defined above.

10. Calibration and Standardization

10.1. Analytical balances are verified each day using routine ARI balance verification procedures specified in ARI SOP 1003S Balance Monitoring, and recorded in a logbook.

10.2. Volumetric devices are verified using routine ARI procedures for verification of volumetric equipment, see SOP 1015S, Pipette Verification.

10.3. Class A volumetric glassware is used and volumetric vessel tubes are certified by the manufacturer for volume accuracy.

10.4. Sulfide standards used for the preparation of Laboratory Control Standards and matrix spiking are standardized using iodometric titration as described in SOP 650S, Sulfide Titration.

11. Procedure

11.1. **Total Aqueous Sulfide**. This procedure is for the measurement of total sulfide in turbid or highly colored aqueous samples. If the sample is not highly colored, excessively turbid or does not contain reducing substances which might interfere with the analysis (e.g. thiosulfate, sulfite) proceed directly to either the iodometric titration (SOP 650S) or the methylene blue colorimetric technique (SOP 653S). The described method will measure dissolved and most complexed sulfides with the exception of some highly insoluble metal sulfides (notably copper, tin and silver complexes).

11.1.1. In general, if the sample is turbid, highly colored or known to contain thiosulfate or sulfite, pre-treatment to remove interferences will be necessary. Pre-treatment could be either further precipitation of sulfide or distillation and trapping in zinc acetate. *Note: ARI typically distills as the preferred pre-treatment for these types of samples.*

11.1.2. The sample should have been preserved with zinc acetate at the time of collection resulting in the formation of a white zinc sulfide precipitate. If an ARI bottle was used for collection, the bottle should be labeled as "Total Sulfide preserved with ZnOAc". If the sample has not been preserved (e.g. samples collected for soluble sulfide), add 2N zinc acetate (2 mL per 500 mL of sample) and adjust to pH >9 using 1M NaOH. Preserved samples must be analyzed within 7 days of sampling.

11.1.3. Precipitation to remove color and or turbidity.

11.1.3.1. This procedure can be used as an alternative to ARI's preferred pre-treatment by distillation.

11.1.3.2. If the sample is highly colored or turbid, precipitate the sulfide with additional zinc acetate and adjust to pH >9.

11.1.3.3. Mark the sample bottle to indicate the "original sample volume" and add an additional 3-4 drops of 2N zinc acetate.

11.1.3.4. Adjust to pH >9 by dropwise addition of 1M NaOH and allow precipitate to settle for 30 minutes.

11.1.3.5. Decant or siphon as much of the supernatant solution as possible without losing any of the precipitate and refill to the "original volume" mark with deoxygenated water.

11.1.3.6. If the sample is still colored or turbid, adjust the pH as necessary and repeat the precipitation. Again decant or siphon the supernatant and refill to the "original volume" mark.

11.1.3.7. If the solution is now clarified, proceed to either the titrimetric or colorimetric analysis on the treated sample. If the level of the precipitate cannot be clearly distinguished or if the sample does not clarify after two repeated precipitations, proceed to the 9030B distillation procedure for releasing the sulfide and trapping it in zinc acetate.

11.1.3.8. Precipitation to concentrate the sulfide. This same procedure can be used to concentrate the sulfide in a low level sample by bring the volume back to a level less than that of the original sample.

11.2. **Soluble (dissolved) Aqueous Sulfide.**

11.2.1. This procedure is for dissolved or soluble sulfide in unpreserved aqueous samples. Samples for dissolved sulfide must be prepared on the day of sample collection or preserved in lab with zinc acetate for preparation the next day. The described procedure will measure dissolved sulfides which remain in solution after precipitation of particulate materials and complexed metal sulfides with aluminum chloride and sodium hydroxide. If the sample is free of turbidity and particulate materials, there is generally no need to run the precipitation and dissolved sulfide will equal total sulfide as determined by either colorimetric or titrimetric procedures. If the sample is turbid or contains particulate materials or precipitates (potential source of complexed sulfides), these must be removed by flocculation-precipitation with aluminum chloride at an alkaline pH (pH 6-9). Precipitation is carried out in a 300 mL BOD bottle. Use care in transferring solutions to minimize aeration of the sample.

11.2.2. Add 0.6 mL 6M NaOH solution to a 300 mL BOD bottle. Carefully fill the bottle with sample using minimum agitation and entrapping no air bubbles.

11.2.3. Add 0.6 mL $AlCl_3$ solution, place stopper in bottle (**NO AIR BUBBLES !!**) and mix by repeatedly inverting the bottle for 1 minute. Additional reagent may be added if absolutely necessary to effect flocculation and precipitation. Solution pH must be maintained between 6 and 9.

11.2.4. Allow precipitate to settle for 5-15 minutes or until a clear supernatant can be drawn off for analysis. Remove the clarified supernatant as soon as is practically possible. Do not allow extended settling times !!

11.2.5. Proceed immediately with the analysis of sulfide using either iodometric titration (for high levels) or the colorimetric procedure.

11.2.6. The analyst must clearly identify that aluminum chloride precipitation has been used. Indicate this on an "Analyst Notes Sheet" along with an additional comment on the actual benchsheet used for finish analysis.

11.3. **Distillation Procedures.** Distillation / extraction is required for all solid phase samples and for those aqueous samples which are highly colored or turbid. Three different procedures for the distillation of sulfide in aqueous and/or solid phase samples are available. The characteristics of the three distillations are shown in Table 1.

11.3.1. For practical application, the procedures have been modified for the use of equivalent glassware in all three methods while retaining the basic chemical and timing conditions required for each. The procedures have been scaled for the use of a 250 mL reaction flask in line with a 125 mL fritted gas washing bottle. Notable differences in the procedure are:

11.3.1.1. The 9030B acid soluble distillation requires a pre-determination of the acid addition necessary to achieve the specified pH conditions (pH <1).

11.3.1.2. The AVS distillation requires knowledge of the water content of the field moist sediment so that the normality of the acid in the dispersing medium will be equivalent for all samples.

11.3.1.3. The PSEP procedure does not discuss the need for dispersing the sample aliquot in the reaction flask.

11.3.2. The need for dispersing the sample aliquot in the reaction flask is discussed in 9030B and is generally applicable to all three procedures. 9030B states, "For an efficient distillation, the mixture in the distillation flask must be of such a consistency that the motion of the stirring bar is sufficient to keep the solids from settling. The mixture must be free of solids that could disrupt the stirring bar."

11.3.3. The determination of dry weight is required for all solid samples. In general, this should be conducted after the sample aliquot has been taking for distillation (avoiding loss due to volatilization). First, gently homogenize the sample and examine for the presence of coarse elements that are not representative of the overall nature of the sample. Such elements can interfere with the stirring of the sample during the distillation and should not be included in the aliquot taken for distillation. Consult with the PM and remove such elements from the sample jar to achieve a more homogeneous matrix. Document such removal on the "Analysts Notes Sheet".

Table 1. Characteristics for sulfide distillation methods

	AVS	**9030 B**	**PSEP**	***ARI***
Reaction Flask (mL)	250	500	1000	***250***
Gas trap	2 X 100-250 mL impingers with non-fritted outlets	125 mL gas washing bottle, fritted outlet	100 mL Nessler tubes	***125 mL gas washing bottle, fritted***
Absorbent	0.2 N (0.1M) zinc acetate	0.2 N (0.1M) zinc acetate	0.2 N (0.1M) zinc acetate	**0.2 N (0.1M) zinc acetate**
Absorbent Volume	2 x 80 mL	115 mL	20 mL	***50 mL***
Dispersing water	100 mL including sediment water content	200 mL	Not defined	***100 mL***
Nitrogen purge (1)	10 min @ 100 ccm	Not defined	10 min	
Sample wt	2 – 10 grams	0.2 to 50 mg sulfide but < 25 grams total weight	Aliquot containing < 50 µg sulfide	***0.5 to 10 grams dependent upon sample***

Nitrogen purge (2)	10 min @ 40ccm	15 min @ 25 ccm	Not defined	***10 min***
Extraction acid	6M HCl, de-aerated	H_2SO_4 conc	Aluminum treated HCL conc	***as per method***
Acid volume	20 mL	Pre-determined + 10 mL	To methyl orange pH (3.1 – 4.4)	***as per method except use of bromphenol blue in PSEP and 10 ml for 9030B.***
Acid concentration	1M or pH < 1	pH ≤ 1	pH < 3.1	***as per method***
Temperature	Ambient	70 °C	90 °C	***as per method except PSEP is 90*** °C
Time	1 hour @ 20 ccm	90 min @ 25ccm	Time to 20 mL distillate (60 min)	***as per method except PSEP is 60 min***

11.3.4. Distillation Log Book. Documentation of the distillation conducted for each sample in a batch is provided by manual entry of the appropriate data to the Sulfide Distillation Log book (ARI 6171F). This form must be completed for each distillation batch at the time the sample processing is being conducted. A distillation batch should not include more than one distillation method. Distillation pre-treatment is required for 9030B to determine acid addition required to attain target pH. A pre-treatment bench sheet is available for printing as needed.

11.3.4.1. Sediment and soil samples may vary in their ability to react with and neutralize the acid added during the distillation. The 9030B acid soluble distillation requires a pre-determination of the acid addition necessary to achieve the specified pH conditions (pH <1) for individual samples such that all samples will be reacted under equivalent pH conditions.

11.3.4.2. PSEP calls for the use of a color indicator to determine a pH <3 in the reaction flask.

11.3.4.3. Pre-treatment: For 9030 B, volume required must be pre-determined by taking an aliquot of the sample equivalent to that which will be used for the extraction, placing it in a beaker and adding DI water to a total volume of 100 mL. Stir and measure the pH. Add concentrated H2SO4 to achieve a pH <1. Note the volume of acid required. Add this pre-determined volume of acid plus an additional 5 mL to the addition funnel. The same procedure is used for turbid aqueous samples.

11.3.5. General Set-up. Assemble the 6 place heating/stirring mantle, glassware (three neck, 250 mL reaction flask, nitrogen inlet adapter, outlet adapter, acid addition funnel) and nitrogen gas train. Close nitrogen valves to the individual reactors and verify the following conditions.

11.3.5.1. The nitrogen tank pressure is less than or equal to 10 psi.

11.3.5.2. The Oxytrap and indicating column are installed in the gas line and are in good condition. The indicator color should be a beige-green; a dark brown color indicates an exhausted column and the column should be replaced.

11.3.5.3. All 24/40 ground glass joints should have Teflon® sleeves installed. The sleeves should be clean and in good condition.

11.3.5.4. Rinse each reaction flask with DI water to remove any acid residue and place a magnetic stir bar in each flask.

11.3.5.5. The nitrogen gas inlet tube extends close to the bottom of the reaction flask (sufficient to extend below the surface of the liquid which will be added to the flask) but not so as to interfere with the movement of the stir bar.

11.3.5.6. Sulfide Gas Traps. Obtain the required number of gas washing bottles and thoroughly rinse each three times with DI water. Clean the frit by forcing pressurized DI water directly from the faucet through the frit tubing. If you detect a sulfide odor during the rinsing process, repeat the rinse (using 0.1N HCl if necessary) until no such odor is observed. The final rinse must be with DI water to remove any acid residuals.

11.3.5.7. If a samples appears to have a high level of sulfide (black, smelly sediment), it is advisable to place two sulfide traps in sequence in order to avoid loss of sulfide due to saturation in the first trap. Carry over of sulfide to the second trap would be evident by the appearance of zinc sulfide cloudiness in the second trap. The contents of the two traps would be combined for the finish analysis.

11.3.5.8. Extraction Acid. Before connecting distillationflask or acid trap add about 60 mL of the required acid to each addition funnel and purge with Nitrogen gas for 10 minutes.

11.3.5.8.1. **PSEP**. Aluminum foil treated HCl (reagent 7.4.1). Add 60 mL of extracting acid to each acid addition funnel. Addition volumes will be based upon changes in the Bromphenol Blue color indicator during the course of the extraction. The change will be from a dark blue to yellow at pH < 3. 20 mL of concentrated acid should be sufficient for most samples.

11.3.5.8.2. **9030 B**. Concentrated H_2SO_4.

11.3.5.8.3. **AVS**. 6N HCl (reagent 7.6.1). Add 20 mL of extracting acid to each acid addition funnel.

11.3.5.9. Add enough 0.2N zinc acetate (reagent 7.4.2) to completely cover the frit of each gas washing bottle. Verify that the glass frit is below the surface of the absorbent.

11.3.5.10. Add 2 drops of bromophenol blue indicator (the color should be dark blue) If the color is green or yellow, acid is present in the flask. In this case, add a few drops of 1N NaOH, disassemble and rinse the apparatus to remove all traces of acid.

11.3.5.11. Connect all system components (nitrogen inlet, acid addition funnel and outlet to gas traps) after the dispersing water has been added to the reaction flask. Turn on the nitrogen supply to the individual reaction flasks by unclamping the acid funnels and clamping the frits with the acid funnel side arms turned open. The acid chamber should be bubbling and adjust nitrogen to equalize the gas bubbling rate within each gas trapping bottle (approximately 5 bubbles /sec). Check each ground glass joint of acid funnel with "Snoop" solution to verify the absence of leaks. Purge at least 10 minutes. Close off the nitrogen supply to the addition funnel by switching the pinch clamp from the frit and replacing it on top of the acid funnel with the side arm closed, then allow the system to purge through the reaction flask for at least 10 minutes.

11.3.5.12. Withdraw the Sample for Analysis. While the system is purging, open the sample jar and gently homogenize to obtain a uniform consistency and incorporation of any overlying liquid. In consultation with the PM, remove any coarse elements that are not representative of the sample. Document such removal on the 'Analysts Notes Sheet' so that it will be plainly evident to ARI< Project Manager.

11.3.5.13. Using the top loading balance, weigh out an aliquot of the homogenized sample onto a piece of tared dissolvable weighing paper (2 to 10 grams, 5 would be most appropriate but do not use less than 2 unless you are certain that sulfide levels are very high). Record the sample weight to 0.001 grams on the Sulfide Distillation Log.

11.3.5.14. Fold and quickly transfer the weigh paper and contained sample to the reaction flask using the outlet port. Insure that all sample gets transferred and that no grit, sand or mud adheres to any portion of the ground glass joint or Teflon sleeve. It is important that no grit particles are lodged within the joint as this will result in gas leaks and low recoveries

11.3.5.15. Dispersing water. Add 100 mL de-oxygenated water to each reaction flask to wash the sample completely into the flask, out of the weight paper, and to ensure glass joint is free of grit.

11.3.5.16. Close the system by inserting the frit back into the reaction flask and keeping the side arm of the acid addition funnel closed to allow the system to purge through the reaction flask for an additional 10 minutes. During this time, verify that the nitrogen inlet tube is below the surface of the liquid in the reaction flask. Adjust the flow of nitrogen to achieve a comparable bubbling rate in all gas washing bottles. Again, you should check all ground glass joints with "Snoop" solution to verify the absence of leaks.

11.3.5.17. Timing and Temperature. While the system is equilibrating prior to acid addition, turn on the magnetic stirrers and heating units as required. Use the pre-determined set points (70 and 90 °C) for temperature control. All distillations should be constantly stirred at a rate that does not create an excessive vortex in the reaction flask, but sufficient enough to keep material suspended. Temperature regimes and timing will vary as shown in the table below

11.3.5.18. **Table 2. Temperature and Timing Conditions.**

Distillation	Temperature (ºC)	Time (minutes)
PSEP	90	60
9030 B	70	90
AVS	ambient	60

11.3.5.19. Once the system has equilibrated to the proper temperature and you have confirmed the absence of leaks, open the acid addition funnel to slowly release the acid into the reaction flask. Begin timing the extraction according to the table above.

11.3.5.20. At the end of the extraction period, quantitatively transfer the zinc acetate trapping solution to a 100 mL Environmental Express vessel, rinsing all trapping solution out with 0.2N zinc acetate, then bring to 100 ml volume. If two traps were used, combine the contents of each and make up to a known volume (150 – 200 mL). Make sure you have entered the final trap volume on the distillation log. The sample is now ready for analysis using either the colorimetric or titrimetric finish procedure.

12. Review

12.1. Not applicable

13. Data Analysis and Calculations

13.1. Not applicable

14. Method Performance

14.1. Not applicable

15. Pollution Prevention

15.1. The procedures discussed in this SOP generate wastes which are hazardous for the characteristic of Corrosivity (RCRA Code D002). These wastes will be collected in a satellite accumulation container and neutralized prior to sink discharge.

15.2. These procedures may also result in the generation and identification of aqueous wastes having sulfide concentrations in excess of 10 mg/L. These will be collected and treated to oxidize contained sulfide prior to sink discharge.

16. Data Assessment and Acceptance Criteria for QC Measure

16.1. Not applicable

17. Corrective Actions for Out of Control Events

17.1. A sample should be re setup for distillations for any of the following problems:

17.1.1. If a leak is detected in the glass joints (not tight fit, or lack of bubbles in reaction flask) then the sample should be re setup and the leaking sample should be discarded.

17.1.2. If it is noticed that the reaction flask lacks a stir bar, or the heat is not turned on then the sample should be re setup.

17.1.3. If the trapping solution is knocked over after distillation than the sample must be reset for distillation.

17.1.3.1. If the sample is prepped the same day then another method blank or LCS is not required for the distillation setup.

17.1.4. If the trapping solution is brought up to a volume over 100 mls, than the excess volume is taken out using a pipette to determine the exact final volume.

17.2. If the samples will not be analyzed the same day than the environmental express vessels containing transferred sample and the standard may be kept in the refrigerator over night. All must be removed in the morning and brought to room temperature before continuing with analysis.

17.3. Record any corrective actions taken on the Yellow Corrective Action form.

18. Contingencies for Handling Out-of-Control or Unacceptable Data

18.1. Not applicable

19. Waste Management

19.1. Reaction flask solutions are acidic wastes (pH <2) and should be collected for neutralization and sink discharge.

19.2. Trapping solutions are caustic (pH >12) and should be collected and neutralized for sink discharge.

19.3. Samples and distillates having sulfide concentrations in excess of 10 mg/L (ppm) should be collected and treated with bleach to oxidize container sulfide prior to sink discharge.

20. Method References

20.1. Standard Method for the Examination of Water and Wastewater On-Line, 2001. 4500-S^{2-} Sulfide.

20.2. EPA 2012. 40 CFR Part 136. "Guidelines Establishing Test Procedures for the Analysis of Pollutants…". Federal Register Friday, March 18, 2012.

20.3. EPA SW-846. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods. Method 9030B. Acid Soluble and Acid Insoluble Sulfides: Distillation.

20.4. Allen, et al.,1991. Determination of Acid Volatile Sulfide and Selected Simultaneously Extractable Metals in Sediment. EPA 821-R-91-100. Draft Analytical Method for Determination of Acid Volatile Sulfide in Sediment.

20.5. Plumb, R. 1981. PROCEDURES FOR HANDLING AND CHEMICAL ANALYSIS OF SEDIMENT AND WATER SAMPLES. Technical Committee on Criteria for Dredged and Fill Material. Environmental laboratory, US Army Engineers Waterways Experiment Station. USEPA/USACOE AD/A103 788.

20.6. PSEP 1986. Conventional Sediment Variables. Total Sulfides. Recommended Protocols for Measuring Conventional Sediment Variables in Puget Sound. USEPA and Puget Sound Water Quality Authority. Modified 2003.

20.7. 40 CFR Part 136, Guidelines Establishing Test Procedures for the Analysis of Pollutants, Appendix B. Definition and Procedures for Determining the Method Detection Limit.

20.8. TNI Interim Standard. 2007. Volume 1, Module 4: Chemical Testing. The NELAC Institute. December 28, 2007

20.9. FACDQ10-13. 2007. DQFAC Single Laboratory DL-QL Procedure (version 2.4). 8/30/2007

21. Appendices

21.1. Sulfide Distillation Log

Appendix 22.1 Sulfide Distillation Log

Analytical Resources,Incorporated
Analytical Chemists and Consultants

Sulfide Digestion Log

Balance ID:	Pretreatment Data							Sample Extraction Data						
Sample ID	Date	Sample Weight	Extract Method*	Acid	Required pH	mL DI Water	Observed mL acid	Date	Sample Weight	mL Acid Required	mL DI Water Required	Trap Volume (mL)	Spike ID	Spike Volume

* Extract Methods: **PSEP** = PSEP; **9030A** = 9030A Acid Soluble; **9030AI** = 9030A acid insoluble; **AVS** = Acid Volatile; **Reactive** = SW-846 reactive

Analyst Name: ______________________________ Date: ________________________ Time: ________________________

6171F
Sulfide Digestion Log

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Revision 003
11/2/12

Aqueou s Sample submitted for Sulfide analysis

21.2. Sediment / soil or highly turbid aqueous samples are acidified under anoxic conditions to release sulfide from the matrix as H_2S. The released H_2S gas is then trapped in either zinc acetate or sodium hydroxide solution to precipitate sulfide (as zinc or sodium sulfide). Finish analysis is conducted on the trapping solution. Three distillation procedures are available: SW-846 Method 9030B (Acid Soluble), PSEP 1986, and Acid Volatile Sulfide (AVS). These vary primarily in the pH and temperature conditions under which the distillation is conducted and do not necessarily release equivalent amounts of sulfide.

Analytical Resources, Incorporated
Analytical Chemists and Consultants

Standard Operating Procedure

Solids Determination

SOP 639S
Version 008.1

Revision Date: 3/23/15
Effective Date: 4/06/15

Prepared by:

Mike Perkins

Approvals:

Casey English, Laboratory Supervisor

Eric Larson, Inorganics Division Manager

Annual Review

SOP Number:	639S
Title:	Solids Determination

The ARI employee named below certifies that this SOP is accurate, complete and requires no revisions

Name	Reviewer's Signature	Date

STANDARD OPERATING PROCEDURES: SOLIDS

1. Scope and Application

1.1. This SOP covers the determination of the solids content of aqueous and solid phase samples.

1.2. The solids content of aqueous samples may be subdivided into a variety of categories based upon physical state and chemical nature. Solids may be present as either dissolved substances or suspended particulates. These may be either organic or inorganic in nature. The separation between the dissolved and particulate phases is operationally defined, usually by filtration through organic free glass fiber filters having a nominal porosity from 1.0 to 2.0 micron (µm). The separation between organic and inorganic solids is accomplished by combustion (ignition) to volatilize the organic fraction.

1.3. The analysis of solid phase samples (soils and sediments) entails drying and/or igniting at uniform temperatures to remove the water and/or volatile materials. Calculations determine the dry weight of material, the residual ash after ignition and the loss on ignition (LOI) or ash-free dry weight.

1.4. This SOP is written to conform to the requirements of Standard Methods on-line Chapter 2540. The specific methods and the older EPA equivalents are shown in the following table.

Analyte	Matrix	EPA 1983	Standard Methods on-line
Total Solids (TS@103–105ºC)	Water	160.3	2540 B-97
Total Dissolved Solids (TDS@180ºC)	Water	160.1	2540 C-97
Total Suspended Solids (TSS@103-105ºC)	Water	160.2	2540 D-97
Fixed and Volatile Solids (TVS@550ºC)	Water	160.4	2540 E-97
Settleable Solids, Volumetric	Water	160.5	2540 F-97
Total, Fixed and Volatile Solids	Solid		2540 G-97

2. Summary of the Procedure

2.1. Analysis is performed by a combination of evaporation, filtration, drying and combustion techniques for known volumes of sample with direct weighing of the residue resulting from any combination of treatments. Drying is generally done at 104°C (102 to 106 °C) to remove all traces of water but higher or lower temperatures may be required for some fractions (e.g. TDS, TOC) to assure that all water has been removed or that components of interest have not been lost through volatilization.

2.2. Ignition or combustion of dried residue is generally performed at 550°C which is sufficient to volatilize organics (and some inorganics) leaving behind an inorganic ash residue. The loss on ignition (LOI, the difference between the dried residue and the ash residue) thus provides an estimate of the amount of organic matter (the volatile solids) originally present in the sample.

2.3. Soil and sediment samples are usually dried at 104°C (102 to 106 °C) in order to provide an estimate of the moisture content (and conversely, the percent solids) of the fresh sample such that the influence of variable water content from sample to sample may be normalized on a dry weight basis. Dried soil and sediment samples may also be ignited at 550°C in order to estimate the organic matter content (volatile solids).

2.4. The Excel benchsheets will automatically perform most of the calculations for the various parameters. Note: calculating cells (i.e. those containing formulas) on the benchsheets are highlighted. With the exception of cells for the evaluation of constant dry weight, these have been protected to prevent alteration of contained formulas.

3. Definitions

3.1. Total Solids. (TS): The total weight of all solid materials (dissolved and particulate) contained per unit weight or volume of sample. For liquids, it is the residue remaining after evaporation of a known volume of homogeneous unfiltered sample expressed in units of mg/L. For soils or sediments, it is the weight remaining after drying a known weight of sample, usually expressed as a percent.

3.2. Total Volatile Solids (TVS): This is the weight of solid material lost upon ignition (combustion) of a dry sample at 550°C. The ash residue remaining after combustion is termed the "fixed" solids component. TVS is expressed per unit volume of fresh sample (mg/L). The "Fixed" component is not normally reported. TVS is also run on soils and sediments where it can be used as a rough approximation of the organic matter content of the sample. Organic matter will usually be overestimated due to losses of structural water (e.g. hydrated aluminosilicates) and decomposition of carbonate minerals upon heating to 550ºC. For soils and sediments, TVS is expressed either per unit dry weight of sample (mg/kg) or as a percent of the dry weight.

3.3. Total Suspended Solids (TSS): Also termed "non-filterable residue", This is the weight of suspended particulate materials (those retained on a filter) per unit volume of aqueous sample (mg/L).

3.4. Total Volatile Suspended Solids (TVSS): This is the volatile component of the TSS that provides an estimate of the organic matter content of the particulates. Again, the ash residue remaining after combustion is termed the "fixed" component. TVSS is expressed per unit volume of aqueous sample (mg/L). The "Fixed" component is not normally reported.

3.5. Total Dissolved Solids (TDS): Also termed "filterable residue", this is the weight of solids remaining after evaporation of a filtered sample. TDS is expressed per unit volume of aqueous sample (mg/L).

3.6. Settleable Solids (SS): This is the amount of suspended solid material settling out of a given volume of sample within a given period of time (45 min + 15 min =1 hour). By definition, it does not include floating materials or "floatable solids". We use the volumetric procedure employing an Imhoff Cone for sedimentation. Units of expression are mL of solid per liter of sample (mL/L).

3.7. Analytical Batch: An analytical batch will consist of twenty (20) or fewer client samples, of the same matrix, processed at the same time by the same analyst. Data for each batch will be recorded on a benchsheet and will include a method blank, a minimum of one sample duplicate plus any additional client requested quality control samples.

3.8. Positive Control – Laboratory Control Sample (LCS): The LCS is used to evaluate the performance of the entire analytical system including all preparation and analysis steps. For aqueous samples, the LCS is a “Quality System Matrix” (reagent water) free from the analyte of interest and spiked with a known amount of inorganic salt or organic polymer. LCS samples are run only for Total Solids, Total Dissolved Solids and Total Suspended Solids The LCS will be run at a minimum of once per analytical batch.

3.9. Negative Control – Method Blank: The Method Blank is used to assess the samples in the analytical batch for possible contamination during the preparation and processing steps. The method blank is run at least once for each preparation batch. The method blank must be processed along with and under the same conditions as the associated samples to include all steps of the analytical process. The method blank shall consist of a “Quality System Matrix” (reagent water) that is free of the analyte of interest.

3.10. Sample Specific Control – Matrix Duplicate: The matrix duplicate is a replicate aliquot of the same sample taken through the entire analytical procedure. The matrix duplicate provides a measure of sample homogeneity and the precision or reproducibility of the analysis when the analyte is present in the matrix. Proper use of the precision evaluation requires that the analyte be present in the sample. Duplicate analysis of non-detect samples provides no information with respect to precision and may sacrifice the detection limit for the sample being analyzed.

4. Interferences

4.1. Heterogeneous samples: Samples must be appropriately mixed prior to withdrawing the aliquot for analysis. Anything, including non-representative artifacts, that will interfere with the ability to take a representative sub-sample must be documented on the analysts “Green Sheet” and discussed with the Project Manager prior to beginning the analysis. <u>Do not exclude any materials from the sample without discussion with the Project Manager</u>.

4.2. Avoid prolonged filtration times and filter clogging for TSS analysis as this will alter the size of particulates retained on the filter. If filtration takes longer than ten minutes, start over using less sample volume. The goal is to have at least 2.5 mg of residue but not more than 200 mg (i.e. residue weight in the range of 0.0025 to 0.200 grams).

4.3. Sample residues for weighing must be at room temperature to avoid convective interference in the balance chamber. This is accomplished by allowing dried to samples to cool to room temperature under desiccation. Desiccation is also required to prevent adsorption of atmospheric moisture.

4.4. Constant dry weight: Accurate solids analysis depends upon achieving a "constant dry weight" for the sample being weighed. For water samples this requires repetition of the "drying-desiccation-cooling-weighing" cycle and is evaluated by observing the difference between successive weighings. This difference must be less than 0.0005 grams (0.5 mg) or 4% of the previous weight (Standard Methods). This will require at least two final weighings for any given sample or parameter.

4.4.1. The Excel spreadsheets have been designed to evaluate constant dry weight criteria between successive weighings. If the difference between two successive weighings is less than 0.0005 grams or 4% of the first weight a “STOP” flag will appear in the next data entry cell. If not, a “reweigh” flag will appear.

4.4.2. Failure to achieve constant dry weight can be attributed to inadequate drying, cooling and/or desiccation. To the extent possible, avoid excessive opening and closing of the desiccator and make sure desiccant has not been exhausted.

4.4.3. Dried samples, particularly ignited ash residues, are notably hygroscopic and may rapidly absorb moisture. Once a sample is removed from the desiccator it should be weighed as soon as possible and returned to the desiccator. Do not allow samples to set out on the lab bench.

4.5. Particular attention must be paid to aqueous samples where the weight of residue obtained will depend upon the volume of sample used and its dissolved solids content. Ideally, filter or evaporate a volume of sample sufficient to provide a residue of at least 2.5 mg but no more than 200 mg (i.e. residue weight in the range of 0.0025 to 0.200 grams). The upper limit of 200 mg is more critical because of the difficulty associated with excessive salt accumulations when removing occluded water and obtaining constant dry weight. The easiest way to evaluate this is by obtaining a conductivity reading on the sample. Higher conductivity values correlate with higher TDS values.

The following table gives approximate volume ranges for aqueous TDS and TS analysis for a given conductivity reading.

Conductivity (µS/cm)	Estimated TDS mg/L	Minimum Volume (mL)	Maximum Volume (mL)
100	65	> 40	< 200
250	162	> 20	< 200
500	325	> 10	< 200
750	488	> 10	< 200
1000	650	> 4	< 200
2500	1625	> 2	< 120
5000	3250	> 1	< 60
10000	6500	> 1	< 30

4.6. Care should be taken if TDS / TS water samples are placed directly in a hot 104°C oven. Samples for TDS and TS analysis should be evaporated at 98ºC in order to avoid splattering, cross contamination and/or blank contamination. Once evaporated, temperature must be increased to the range of (102 to 106 °C) or 180 ±2ºC.

5. Safety

5.1. The toxicity or carcinogenicity of each reagent used in this SOP has not been precisely defined. Treat each chemical compound as a potential health hazard. Reduce exposure to all chemicals to the lowest possible level by whatever means available.

5.2. Environmental Samples may contain hazardous materials; treat them as potential health hazards.

5.3. Use CAUTION with strong irritants such as acids, bases. Avoid breathing the fumes of these irritants by using them in a hood when possible and keeping the face away from open containers of these chemicals. Avoid contact of these irritants with skin and clothing by appropriate use of gloves, apron, face–mask, hood shield, etc. Safety glasses must be worn all the time in the Lab.

5.4. Dispose of all unwanted, broken glassware into a broken glassware container. Inspect every piece of glassware. Do not use any that are chipped, cracked, etched, or scratched. Glassware with minor damage should be stored for repair.

6. Equipment and Supplies

6.1. Glass Fiber Filters (TDS) (Millipore AP40 (Fisher # AP4004705), Gelman Type A/E or equivalent): These are organic binder free 47mm glass fiber filters with a porosity of 0.7µm. The filters should be pre-washed with deionized water (3 times 20 mL) and pre-dried at 104°C.

6.2. Glass Fiber Filters (TSS & TVSS). Environmental Express ProWeigh Filters (ProWeigh Filters, Catalog #'s F93447MM and F93447VOL). These are binder-less, pre-washed and pre-weighed, 47 mm glass fiber filters having a nominal porosity of 1.5 µm. Each filter comes in an aluminum pan that is individually numbered along with the pre-determined filter weight (to 4 places). Filters identified as F93447VOL have been pre-combusted and are used for the analysis of Total Volatile Suspended Solids (TVSS).

6.3. Filtration Apparatus, 47mm: Pall-Gelman #4247 magnetic, 300 mL capacity (or equivalent)

6.4. Porcelain Evaporating Dishes (TS, TVS, TDS): 10, 20, 50, 100 and 150 mL (Fisher #S337051CR) and 250 mL (Fisher #S33706CR) capacity dishes pre-dried at 180°C and stored under desiccation. If volatile solids are to be determined, the dishes must be pre-combusted at 550°C and stored under desiccation.

6.5. ALUMINUM WEIGHING DISHES (SOILS & SEDIMENT dry weight) Pre-dried at 104°C. Do not use these dishes for the determination of TDS.

6.6. DRYING OVENS Gravity or mechanically convected, adjustable to 200°C: Gravity convection is preferred for the drying of samples since mechanically convected ovens can create drafts that could displace dried materials from their containers. Mechanically convected ovens should only be used for drying of equipment and materials used for the analysis.

6.7. Muffle Furnace suitable for operation at 550ºC.

6.8. Desiccators. Desiccators are used for cooling heated samples to room temperature in a moisture free atmosphere. They are also used for storing pre-weighed materials such that they will not absorb moisture from the atmosphere. Desiccators must be provided with effective color-indicating desiccant. Indicating Drierite, calcium sulfate impregnated with cobalt chloride, is preferred (Fisher # 07-578-3A). If the Drierite (or other indicator) has turned from blue to red or pink, it has been exhausted and should be restored or replaced with effective material. See instructions on bottle of Drierite for restoring the desiccant. There is also a supply of color indicating (cobalt chloride impregnated) silica gel desiccant beads (Fisher # S162-212) that can be used for verifying effectiveness of the desiccant being used.

6.9. Analytical balance: The balance used must be capable of measurement to 4 places (0.0001 g). Balance verification is accomplished using ASTM E 617-97 traceable weights. The benchsheet for each solids parameter contains space for the entry of balance calibration verification data that must be completed at the beginning of each weighing cycle. The calibration weight must return a value within 1 mg or 10% of its known weight, whichever is less.

6.10. Weights for balance verification: Troemner Calibration weights, ASTM E 617-97 traceable (equivalent to old NBS Class S and S-1 standards). Each weight set is certified every five years by an outside metrologist. A certificate documenting the "true" weight of each calibration weight accompanies each set.

7. Reagents and Standards

7.1. TDS and TS Verification Standard: The standard used is equivalent to the 442 Natural Water Standard typically used for calibration of TDS meters (Myron L Company) but is diluted to value less than 1000 mg/L. It is prepared at concentrations of 20% sodium sulfate, 20% sodium bicarbonate and 10% sodium chloride by dissolving 0.8 grams of sodium sulfate (Na_2SO_4), 0.8 grams of sodium bicarbonate ($NaHCO_3$) and 0.4 grams of sodium chloride (NaCl) in 4 liters of deionized water yielding 500 mg/L TDS. Record the preparation data (identification and weight of each salt used and the final volume of prepared standard) in the "Standards Preparation Logbook" and label the prepared bottles with the ARI Identification number, the date of preparation and the calculated TDS/TS concentration.

7.2. TSS Verification Standard: This standard is prepared by adding 50 mg (0.05 g) of Cellulose powder (MP Biomedicals, Cellulose Powder, Microcrystalline #191499, Fisher Catalog # ICN19149980, 100 gram quantity) to 1000 mL of DI water. The standard is prepared fresh for each analytical batch. At least one TSS verification standard will be prepared and analyzed for each analytical batch. Record the source of the cellulose powder, the actual grams weighed and the volume of solution prepared on the Excel benchsheet.

8. Sample Collection, Preservation, Shipment and Storage

8.1. Samples may be collected in glass or plastic bottles provided that no materials adhere to the container walls. If materials are observed to be adhering to the container wall, notify PM and document on an Analysts Greensheet.

8.2. Refrigerate sample at 4ºC up to the time of analysis to minimize microbial decomposition of solids.

8.3. Begin analysis as soon as possible (within 24 hours) but no later than seven (7) days. Settleable solids should be determined within 48 hours (EPA 2012 MUR).

8.4. Sub-sampling is a critical component of solids analysis. In order to obtain accurate and reproducible results, be certain that the sample is well mixed and that the particulates are uniformly distributed throughout the sample prior to withdrawing the aliquot.

8.5. Prior to beginning a solids analysis for an aqueous sample, ascertain what other parameters are required for that sample and be sure to reserve sufficient sample for the completion of those analyses. It is quite easy to totally exhaust a sample for the analysis of TSS and have nothing left for the analysis of other parameters which may be required. Check with your supervisor!

Whenever possible, use the same sample aliquot for multiple determinations (e.g. TSS and TDS can come from the same sub-sample).

8.6. Occasionally ARI will receive multiphase heterogeneous samples. Do not process multiphase samples without specific, documented instructions from ARI's Project Manager or Client. Note: When conducting an environmental investigation, the investigator generally has some specific purpose in mind. He/she then designs and executes a sampling program oriented toward providing information relative to that specific purpose. One goal of environmental sampling is that the sample be representative of either the environment from which it was taken or some specific characteristic of interest. Any unbiased environmental sample has the potential to contain materials (rocks, biological material, multiple phases etc.) that are non-representative of either the matrix or the characteristic. Such materials will often be excluded or separated from the sample when they are judged to be irrelevant to the specific purpose of the investigation or the characteristic of interest. A fundamental principle of environmental sampling is that only the designer of the sampling program makes decisions concerning the representativeness of materials contained within a sample. That person makes the decision to exclude materials from the sample. When a sample arrives at the laboratory, ARI can only assume that it represents the specific purpose and desires of the investigator. Decisions as to the exclusion of materials or separation of phases have already been made by the investigator and sampling personnel. It is not the role of ARI personnel to exclude materials or phases from a sample for analysis unless it is done with the knowledge and under the specific direction of ARI's client.

9. Quality Control

9.1. Balance Verification. Each analytical balance is verified against ASTM E 617-97 traceable (NTIS equivalent to older NBS Class S and S-1 standards) weights at the beginning each weighing cycle.

9.2. Negative Control – Absence of contamination. Negative control is provided by the analysis of a method blank that has been processed along with and under the same conditions as associated samples. The Method Blank will consist of deionized water. One method blank is processed along with each analytical batch of 20 or less samples.

9.3. Positive Control – Recovery of known concentrations of solids. Positive Control for aqueous TDS, TS and TSS is provided by the analysis of a Laboratory Control Sample (LCS) that has been processed along with and under the same conditions as associated samples. The TDS standard consists of a solution containing known weights of dissolved inorganic salts while the TSS standard consists of a known weight of organic particulates (microcrystalline cellulose) in a known volume of DI water. At least one LCS standard is processed along with each analytical batch of 20 or less samples.

9.4. Matrix Specific Control: Method performance with respect to the sample matrix will be conducted by the analysis of matrix duplicates. The matrix duplicate provides a measure of the precision (repeatability) of the analysis. Proper use of the precision evaluation requires that the analyte be present in the sample. Duplicate analysis of non-detect samples provides no information with respect to precision.

10. Calibration and Standardization

10.1. Each analytical balance has an internal calibration sequence that is conducted daily and then verified against ASTM E 617-97 traceable (NTIS equivalent to old NBS Class S and S-1 standards) weights covering the range of determination.

10.2. The balance is verified prior to each weighing cycle. Space is provided on the benchsheets to record the Identification of the weight set used and the date and time of verification.

11. Procedure

11.1. **Total & Total Volatile Solids**. A well-mixed sample aliquot is withdrawn and evaporated to dryness at 102 to 106°C. The weight of dried residue is determined and expressed relative to the volume or weight of sample used. If the volatile component is desired, the dried residue is then ignited at 550°C and then re-weighed. The loss on ignition represents the volatile component which again is expressed relative to the initial sample volume or weight.

11.1.1. Sample Analysis, Aqueous samples

11.1.1.1. Obtain a blank benchsheet for Aqueous TS/TVS and record all handwritten raw data. Under the "Tare Wt" Column, enter the calibration weight set ID (CV-02 in most cases), the date & time and the observed calibration weight value (using a 100 gram calibration weight). The calibration weight must return a value within the range of 100 ±0.1. If it does not, re-calibrate the balance and repeat the verification before continuing.

11.1.1.2. Review the job folder and check for any possible special client instructions that might require additional quality control samples, special reporting limits, or special sample handling.

11.1.1.3. Obtain a clean dry porcelain evaporating dish. If volatile solids are to be determined, the dish should be pre-combusted at 550°C. Record the number and tare weight (in grams to 4 places) of the evaporating dish on the benchsheet (Do not touch dishes with your fingers, use the dish tongs).

11.1.1.4. Obtain a conductivity reading on an aliquot of the sample and determine the appropriate volume of sample to evaporate from the table in Section 4.6. The volume will depend upon the solids content in the sample. If the solids content is suspected to be high, a smaller volume may be used. The goal is to eventually obtain at least 2.5 mg of dried residue in the evaporating dish but not more than 200 mg.

11.1.1.5. Mix the sample to homogenize and withdraw the volume (mL) required to achieve a residue weight in the range of 2.5 to 200 mg. If volatiles are to be determined double the volume evaporated.

11.1.1.6. Transfer the selected volume of unfiltered sample to the evaporating dish and evaporate at 98°C. Close inspection will be required to ensure that the samples do not boil and splatter causing loss of sample or cross contamination. Once evaporated, increase temperature to a range of (102 to 106 °C) and dry for at least 1 hour.

11.1.1.7. Upon completion of the evaporation, perform the initial dry weight determination. Remove the dish from the oven and transfer to a desiccator for cooling to room temperature (approximately 2 hours). Record the balance calibration verification data. Weigh the dish after the initial evaporation and add more sample if the initial residue weight is less than 2.5 mg. Proceed to the final drying if the residue weight is greater than 2.5 mg. Be sure to record any additional volume added and repeat the evaporation as necessary.

11.1.1.8. After the final evaporation, remove the dish from the oven and place in a desiccator and cool to room temperature (approximately 2 hours).

11.1.1.9. Repeat the balance verification data entry. Determine the weight of the cooled dish and record it on the benchsheet. Return the dishes to the drying oven for an additional hour and then repeat the verification, cooling and weighing process. Formulas in the spreadsheet will evaluate the difference between successive weighings. If the weight loss is < 0.0005 grams or 4% of the first weighing (whichever is less), the analysis is complete and the next data entry cell will have a "STOP" flag. If the weight loss is > 0.0005 grams or 4% of the first weighing, the next data entry cell will indicate "reweigh". Repeat the drying cooling process until the 0.0005 gram criterion is satisfied. There is space for only three weighings on the benchsheet. Note any failure to achieve constant dry weight on the Analysts Green Sheet.

11.1.1.10. For each batch of 20 or less samples, process at least 1 duplicate, 1 LCS and a method blank. Additional quality control samples may be required by the client. Be sure to check the job folder for any special instructions. Record all data and notes on the benchsheet and enter the data into the computer spreadsheet. The handwritten benchsheet along with the computer calculated data is turned in for review. Any anomalies, sample artifacts, or analytical problems should be noted on the "Analysts Green Sheet" in the appropriate job folder.

11.1.1.11. If volatile solids are required, transfer the dish to the muffle furnace preheated to 550°C. Allow 15 to 20 minutes for combustion and then remove the dish to a desiccator for 1 hour or until cooled to room temperature. Make at least 2 successive weighings of the cooled sample to confirm a constant weight. The benchsheet will again evaluate for constant dry weight. When the ash weight is greater than the dry weight (±5%), a "check for Error" message appears. Something is wrong, evaluate your weighing

11.1.2. Sample Analysis. Soil and Sediment Samples

11.1.2.1. Obtain a blank benchsheet for TS/TVS in Soils and record all handwritten raw data. Under the "SAMPLE (grams)" Column, enter the calibration weight set ID (CV-02 in most cases), the date & time and the observed calibration weight value (using a 10 gram calibration weight). The calibration weight must return a value within the range of 10 ±0.001. If it does not, re-calibrate the balance and repeat the verification before continuing.

11.1.2.2. Review the job folder and check for any client special instructions that might require additional quality control samples, special reporting limits, or special sample handling.

11.1.2.3. Obtain an aluminum weighing dish (embossed with an identification number). Determine and record its tare weight under the "TARE WT" column. Weigh out 5 to 10 grams of sample and transfer to the pre-weighed dish. Record the exact weight of sample under the "SAMPLE (grams)" column (in grams to 4 places). Record the date and time the sample is placed in the oven into the "Batch Drying Time" box of the benchsheet using an "mm/dd/yy 00:00" date/time format. Transfer the dish to a drying oven set at 104°C (102 to 106 °C) and allow to dry overnight (12-24 hours).

11.1.2.4. Remove dish from oven, record the date and time removed in the "Batch Drying Time" box, and transfer to a desiccator. Cool to room temperature. Record the balance calibration verification data. Determine the weight of the cooled dish and record it on the benchsheet.

11.1.2.4.1. In the event that the sample was in the oven for less than 12 hours, it must be documented that constant weight was attained. This is accomplished by performing a minimum of two repetitive “drying-desiccation-cooling-weighing” cycles with a minimum of 1-hour drying time in each cycle. Constant weight is achieved if there is a loss in weight of no greater than 0.01 grams between the start weight and the final weight of the last cycle. There is space on the benchsheet for entry of this data if necessary. The third dry weight column contains a formula which will test for the 0.01 gram difference.

11.1.2.5. For each batch of 20 or less samples, process at least 1 duplicate and a method blank. Additional quality control samples may be required by the client. Be sure to check the job folder for any special instructions. Record all data and notes on the benchsheet and enter the data into the computer spreadsheet. The handwritten benchsheet along with the computer calculated data is turned in for review. Any anomalies, sample artifacts, or analytical problems should be noted on the "Analysts Notes" form in the appropriate job folder.

11.1.3. If volatile solids are required, transfer the dish to the muffle furnace preheated to 550°C. Allow 30 minute combustion time and then remove the dish to a desiccator for 15 minutes or until cooled to room temperature (ashed samples will rapidly absorb moisture from the air, do not leave combusted samples sitting out in the open!). Do not run the temperature above 550°C in order to avoid volatilizing the aluminum dish. Make at least 2 successive weighings of the cooled sample to confirm a constant weight.

11.2. **Total Suspended & Total Volatile Suspended Solids (TSS & TVSS)**. A well mixed sample aliquot is withdrawn and filtered through a pre-weighed glass fiber filter. The dry weight of material retained on the filter is determined and then expressed relative to the volume of sample filtered as TSS in mg/L. Weight loss on combustion represents the volatile component which is again expressed relative to the volume of sample filtered as TVSS in mg/L. The filtrate from the TSS determination can be used for the analysis of total dissolved solids (TDS) if requested.

11.2.1. Sample Analysis

11.2.1.1. Obtain a blank benchsheet for Aqueous TSS/TVSS and record all handwritten raw data. Enter the calibration weight set ID (CV-02 in most cases), the date & time and the observed calibration weight value (using a 10 gram calibration weight). The calibration weight must return a value within the range of 10 ±0.001. If it does not, re-calibrate the balance and repeat the verification before continuing. Use the "Tare Wt." Column to enter the pre-determined weight of the filters used for analysis (when using either the ProWeigh standard or volatile filters).

11.2.1.2. Review the job folder and check for any possible special client instructions that might require additional quality control samples, special reporting limits, or special sample handling.

11.2.1.3. Setup the filtration apparatus and place a pre-washed, dried and weighed filter, rough side up, on the base. The Environmental Express ProWeigh filters are contained in aluminum weighing pans that have been labeled for easy identification. Filters should be handled only with forceps. Record the weighing pan number and the tare weight of the filter as shown on the Mylar label (in grams to 4 places using the "TARE WT" column of the benchsheet for the weight).

11.2.1.3.1. If TVSS is being determined, you must use the ProWeigh Volatile filters (Environmental Express F93447VOL). They have been pre-combusted at 550ºC and pre-weighed.

11.2.1.4. Mix the sample and filter 100 to 1,000 mL. The volume filtered will depend upon suspected solids content in the sample. If the solids content is suspected to be high (noticeable turbidity), a smaller volume may be filtered. In general, if the filtration time is greater than 10 minutes use a smaller filtration volume. The goal is to obtain at least 2.5 mg of dried residue on the filter for a maximum of 1,000 mL filtered. Make sure that there is sufficient sample for all analyses which may be required aside from TSS.

11.2.1.5. Rinse the filter with three successive 10 mL portions of DI water allowing complete drainage between washings.

11.2.1.6. Continue to apply vacuum for at least one minute after all sample has passed the filter to completely remove any residual water. The filter should be as dry as possible in order to prevent the filter from sticking to the drying pan. This is very important!! Transfer the dish and filter to the drying oven set at 104°C (102 to 106°C) and dry for 1 hour. Remove and allow to cool to room temperature in a desiccator.

11.2.1.7. Verify balance calibration prior to beginning each weighing cycle. Enter the identification of the calibration verification weight set, the date and time, and the observed calibration weight value (using a 10 gram calibration weight). The calibration weight must return a value within the range of 9.999 to 10.001. If it does not, re-calibrate the balance and repeat the verification before continuing.

11.2.1.8. Remove the cooled filter from the dish and determine its weight. Record it on the benchsheet. Return the dish and filter to the drying oven for an additional hour and then repeat the verification, cooling and weighing process. Formulas in the spreadsheet will evaluate the difference between successive weighings. If the weight loss is < 0.0005 grams or 4% of the first weighing (whichever is less), the analysis is complete and the next data entry cell will have a "STOP" flag. If the weight loss is > 0.0005 grams or 4% of the first weighing, the next data entry cell will indicate "reweigh". Repeat the drying cooling process until the 0.0005 gram criterion is satisfied.

11.2.1.9. If volatile solids are required, transfer the dish and filter to the muffle furnace preheated to 550°C. Allow a 15 minute combustion time (assuming a maximum 200 mg residue) and then remove the dish to a desiccator for 15 minutes or until cooled, do not leave the ashed sample sitting out in the open. Make at least 2 successive weighings of the cooled sample to confirm a constant weight. Formulas in the spreadsheet will again evaluate the difference between successive weighings. Repeat the drying cooling process until the 0.0005 gram criterion is satisfied.

11.2.1.10. For each analytical batch, process at least 1 duplicate, 1 LCS and a method blank. However, it is not advisable to duplicate non-detect samples in that such duplication provides no information with respect to precision and may sacrifice the detection limit for the sample analyzed. Try to use a sample that has noticeable particulates.

11.2.1.11. Additional quality control samples may be required by the client. Be sure to check the job folder for any special instructions. Record all data and notes on the benchsheet and enter the data into the computer spreadsheet. The handwritten benchsheet along with the computer calculated data is turned in for review. Any anomalies, sample artifacts, or analytical problems should be noted on the "Analysts Notes" form in the appropriate job folder.

11.3. **Total Dissolved Solids**. This procedure provides a measure of the total dissolved salts within a water sample in lieu of a complete chemical analysis. Particulate materials are removed from the sample by filtration through a standard filter (e.g. Millipore AP40 or equivalent) and the resulting filtrate (whole volume) is evaporated to dryness at 98°C followed by a final drying at 180 ±2°C to remove any occluded water. The weight of the dried residue is determined and expressed relative to the original volume of sample evaporated (in mg/L). Care needs to be taken to ensure that the sample does not boil and splatter during the initial evaporation.

11.3.1. Sample analysis

11.3.1.1. Obtain a blank benchsheet for Aqueous TDS and record all handwritten raw data. Enter the calibration weight set ID (CV-02 in most cases), the date & time and the observed calibration weight value (using a 100 gram calibration weight). The calibration weight must return a value within the range of 100 ±1.0 (99 to 101 grams). If it does not, re-calibrate the balance and repeat the verification before continuing.

11.3.1.2. Review the job folder and check for any possible special client instructions that might require additional quality control samples, special reporting limits, or special sample handling.

11.3.1.3. Obtain a clean dry porcelain evaporating dish. If volatile solids are to be determined, the dish should be pre-combusted at 550°C. Record the number and tare weight (in grams to 4 places) of the evaporating dish on the benchsheet (Do not touch dishes with your fingers, use the dish tongs).

11.3.1.4. Setup the filtration apparatus with a clean, DI rinsed vacuum flask and filtration funnel. Place a glass fiber filter (Millipore AP40 or equivalent) on the base and rinse with

3 successive 20 mL washings of DI as necessary (i.e. the filters have not been pre-washed). Continue suction to remove all traces of water and then discard the washings.

11.3.1.5. Obtain a conductivity reading on an aliquot of the sample and determine the appropriate volume of sample to evaporate from the table in Section 4.6. The volume will depend upon the solids content in the sample. If the solids content is suspected to be high, a smaller volume may be used. The goal is to eventually obtain at least 2.5 mg of dried residue in the evaporating dish but not more than 200 mg.

11.3.1.6. Mix the sample and withdraw the volume required to provide a residue weight of 2.5 to 200 mg or a total volume of no more than 200 mL. Filter the selected volume and wash with three (3) successive volumes of DI water. The entire volume filtered, including the washings, must be evaporated.

11.3.1.7. Record the number and tare weight (in grams to 4 places) of the evaporating dish on the benchsheet (Do not touch dishes with your fingers, use the dish tongs). Transfer 100 mL of filtrate+washings (or the volume selected from the table in 4.6) to the evaporating dish and evaporate at 98°C. Record the volume of original sample addition.

11.3.1.8. As necessary, add the remaining filtrate+washings to the same evaporating dish and continue until all filtrate+washings have been evaporated. Record the added volume.

11.3.1.9. After final evaporation, transfer the dish to the drying oven set at 180 ±2°C and bake for 1 hour. Remove and cool to room temperature in a desiccator. Making sure the desiccant has not been exhausted. The upper weight limit for the residue is 200 mg. If there are more than 200 mg of residue, re-analyze the sample using a smaller aliquot.

11.3.1.10. Determine the weight of the cooled dish and record it on the benchsheet. Return the dishes to the drying oven for an additional hour and then repeat the verification, cooling and weighing process. Formulas in the spreadsheet will evaluate the difference between successive weighings. If the weight loss is < 0.0005 grams or 4% of the first weighing (whichever is less), the analysis is complete and the next data entry cell will have a "STOP" flag. If the weight loss is > 0.0005 grams or 4% of the first weighing, the next data entry cell will indicate "reweigh". Repeat the drying cooling process until the 0.0005 gram or 4% criterion is satisfied.

11.3.1.11. For each batch of 20 or less samples, process at least 1 duplicate, 1 LCS and a method blank. Additional quality control samples may be required by the client. Be sure to check the job folder for any special instructions. Record all data and notes on the benchsheet and enter the data into the computer spreadsheet. The handwritten benchsheet along with the computer calculated data is turned in for review. Any anomalies, sample artifacts, or analytical problems should be noted on the “Analysts Notes” form in the appropriate job folder.

11.4. **Settleable Solids.** This is the amount of solid material settling out of suspension from a given volume of sample within a given period of time (45 min + 15 min =1 hour). By definition, it does not include floating materials or "floatables". We use the volumetric procedure employing an Imhoff Cone for sedimentation. Units of expression are mL of solid per liter of sample (mL/L).

11.4.1. Sample analysis

11.4.1.1. Obtain a blank benchsheet for Settleable Solids (ARI #6055). Use this to record all handwritten raw data.

11.4.1.2. Obtain the 1-liter Imhoff cones and cone rack. We have two sets of 3 cones. One reads to 0.5 mL while the other reads to 0.1 mL. Use the 0.1 mL cones.

11.4.1.3. Mix the sample to homogeneously distribute any particulate materials and then pour up to 1 liter into the Imhoff cone. Record the volume (mL) of sample used.

11.4.1.4. Allow initial settling for 45 minutes. After initial settling, **gently** re-suspend any solids adhering to the side of the flask using a glass stir rod or by gently swirling the cone. Use caution so as not to spill any sample while swirling. Allow to settle for an additional 15 minutes.

11.4.1.5. Read the mL of settled volume from the scale on the bottom of the cone.

11.4.1.6. If there are voids of clear liquid in and between the larger settled particles, estimate the volume of these voids and subtract from the total settled volume.

12. Review

12.1. Supervisor reviews Service Request, and assigns analysis and communicates any special instructions to the analyst.

12.2. Analyst reviews Service Request and any special instructions, obtains the appropriate benchsheet and proceeds with the analysis. A handwritten benchsheet is generated and the data are then entered into the computer for data reduction.

12.3. Creation of Worklists. The final computer generated result is placed into the method folder in chronological sequence and a copy is placed into the job folder. The data undergo supervisor review and the analysts then enters the data into LIMs to create the worklist.

12.4. Distribution of worklists. The supervisor reviews the LIMs input, distributes acceptable data and returns the analysis package to analyst for placement in the job folder.

12.5. The supervisor reviews the job folder for completeness of analysis (all requested parameters have been run) and sufficiency of Quality Control.

12.6. The completed analysis package is then reviewed by the Conventionals QA Reviewer and the final report printed.

12.7. The final report is reviewed for accuracy and completeness, signed by the Conventionals QA reviewer and delivered to the Project Manager for final disposition to the client.

13. Data Analysis and Calculations

13.1. With the exception of Settable Solids, all analyses are gravimetric determinations in which a determined dry weight of solid residue is expressed relative to the volume or mass of sample used to obtain that residue. Specific calculations on the Excel spreadsheets are as follows:

13.2. Total Solids, aqueous

dry weight (mg) = (minimum observed grams – tare grams) x 1,000

Total Solids (mg/L) = dry weight / mL sample X 1,000

If dry weight < 1mg, flag as "<" 1mg / mL sample X 1,000

13.2.1. Total Volatile Solids (TVS), aqueous,

ash weight (mg) = (minimum observed grams – tare grams) X 1,000

TVS (mg/L) = (dry weight –ash weight) / mL sample X 1,000

If (dry weight - ash weight) < 1 mg, flag as "<" 1 / mL sample X 1,000

13.3. Total Solids, solids

dry weight (g) = (minimum observed grams – tare grams)

Total Solids (%) = dry weight / grams sample X 100

13.3.1. Total Volatile Solids (TVS), solids

ash weight (g) = (minimum observed grams – tare grams)

TVS (mg/kg) = (dry weight –ash weight) / dry weight X 1,000,000

TVS (% dry weight) = (dry weight – ash weight) / dry weight

If (dry weight – ash weight) < 1 mg, flag as "<" 1 / grams dry weight X 1,000

13.4. Total Suspended Solids

dry weight (mg) = (minimum observed grams – tare grams) X 1,000

TSS (mg/L) = dry weight (mg) / mL sample X 1,000

If dry weight < 1 mg, flag as "<" 1/mL sample X 1,000

13.4.1. Total Volatile Suspended Solids (TVSS)

ash weight (mg) = (minimum observed grams – tare grams) X 1,000

Loss on ignition (LOI) = dry weight – ash weight

TVSS (mg/L) = LOI / mL sample X 1,000

If LOI < 1 mg, flag as "<" 1 / mL sample X 1,000

13.5. Total Dissolved Solids

dry weight (mg) = (minimum observed grams – tare grams) X 1,000

TDS (mg/L) = dry weight / mL sample (original + added) X 1,000

If dry weight < 1 mg, flag as "<" 1/mL sample X 1,000

13.6. Settleable solids are calculated as

Settleable Solids (mL/L) = Settled Volume mL / Sample Volume mL X 1,000

13.7. For Duplicate analysis, the relative percent difference (RPD) is calculated as:

RPD = ABS[original – duplicate] / average (original, duplicate) X 100

14. Method Performance

14.1. Total Solids-soils and sediments: Approximately 5 grams of sample are typically taken for analysis. Weighing is conducted on a 4 place analytical balance. While the balance reports to 0.1 mg, a sensitivity of 1 mg is routinely used to set reporting limits. This yields a reporting limit of 0.02% for solids analysis. The mean of control chart blanks averages -0.1 mg with an upper control limit (the mean +3 standard deviations) of 0.4 mg.

14.2. Total Solids-aqueous samples: Using the same weighing criteria as for soils and sediments, a 1 mg residue limit with a maximum evaporation volume of 200 mL provides a reporting limit of 5 mg/L. The analysis is not run often enough to have created control charts for the determination.

14.3. Total Dissolved Solids: The 1 mg residue detection limit coupled with a maximum evaporation volume again yields a reporting limit of 5 mg/L. Recovery of the 500 mg/L LCS averages 93.3% (466 mg/L) with 3 standard deviation control limits of 91 to 108%. Blanks average 2.2 mg/L with an upper control limit (3 standard deviations) of 14 mg/L.

14.4. Total Suspended Solids: The one mg residue limit with a maximum filtration volume would yield a reporting limit of 1 mg/L. Recovery of the 50 mg/L LCS averages 99.1% (49.6 mg/L) with 3 standard deviation control limits of 97 to 101%. Blanks average 0.0 mg/L with an upper control limit (+3 standard deviation) of 0.2 mg/L.

15. Pollution Prevention

15.1. Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. The quantity of chemicals purchased should be based on expected usage during their shelf life to reduce disposal cost of unused material. Actual reagent preparation volumes should reflect anticipated usage and reagent stability.

16. Data Assessment and Acceptance Criteria for QC Measure

16.1. Blank determinations must return residue weights less than 1 mg.

16.2. Laboratory Control Sample (LCS) determinations must return values within 10% of their known concentrations.

16.3. Replicate RPD's should be less than 20%.

17. Corrective Actions for Out of Control Events

17.1. If holding times (7 days) have been exceeded or if there is insufficient sample to run the analysis, the supervisor will be immediately notified. The supervisor will inform the project manager for resolution with the client and all information will be recorded on the "Analysts Notes" form.

17.2. If the weight loss between successive dryings for aqueous samples is greater than 0.0005 grams or 4%, the sample will be re-dried at 104°C for 1 hour, cooled in a desiccator and re-weighed. This will be repeated as necessary to obtain the 0.0005 gram criterion. If less than 12 hours of oven drying has been used for soils, constant dry weight will be documented using a 0.01 gram criterion.

17.3. If the residue weight for TDS analysis is greater than 200 mg, the analysis will be repeated using a smaller sample aliquot.

17.4. If the duplicate RPD is outside the prescribed limits, the PM will be notified to make a decision on whether the sample will be reanalyzed to verify out of control RPD. This corrective action and any observations will be clearly documented on the "Analysts Notes" form.

17.5. If the method blank value exceeds either 1 mg or the reporting limit the entire batch may require reanalysis. Check for obvious data entry errors and compare the blank value to the samples. If the sample values are greater than 10X the blank no further corrective action is required. If the sample values are < 10X the blank value inform the appropriate project manager and have them contact the client for necessary corrective action, samples may require reanalysis. Make sure to document all corrective actions and observations on the "Analysts Notes" form

18. Contingencies for Handling Out-of-Control or Unacceptable Data

18.1. Any analytical batch or sample not satisfying the above criteria will be documented as to probable cause and discussed with the Project Manager.

18.2. Re-runs will be conducted at the discretion of the Project Manager.

18.3. The analytical batch will not be controlled by the duplicate RPD.

19. Waste Management

19.1. There are no hazardous chemicals associated with this procedure.

19.2. Samples are held until final reports have been issued. Samples may contain RCRA hazardous constituents and these are screened in our LIMs system. Samples which LIMS identified as containing one or more hazardous constituents will be segregated into identified waste profiles and disposed of through our RCRA TSD (Treatment, Storage Disposal facility). Samples not having identified hazardous constituents will be sink disposed.

20. Method References

20.1. Standard Methods 2540 Solids, Standard Methods on-Line, Standard Methods for the Examination of Water and Wastewater

20.2. Methods for the Chemical Analysis of Water and Wastes, EPA-600/4-79-020 (Rev March 1983).

20.3. EPA Method Update Rule (MUR), 2012, 40 CFR Part 122, 136, et al. “Guidelines Establishing Test Procedures for the Analysis of Pollutants…” Federal Register May 18, 2012.

Analytical Resources, Incorporated
Analytical Chemists and Consultants

Standard Operating Procedure

Ammonia, Auto-phenate

SOP 615S
Version 006

Revision Date: 3/29/17
Effective Date: 3/29/17

Prepared by:

Mike Perkins

Approvals:

Casey English, Laboratory Supervisor

Eric Larson, Inorganics Division Manager

Annual Review

SOP Number: 615S

Title: Ammonia, Auto-phenate

The ARI employee named below certifies that this SOP is accurate, complete and requires no revisions

Name	Reviewer's Signature	Date

Standard Operating Procedures: Ammonia, Auto-phenate

1. Scope and Application

1. This method is for the determination of ammonia nitrogen (NH_3-N) in drinking, surface, domestic and industrial wastes and saline (2M KCl) soil extracts using automated phenate, flow injection analysis (FIA). The procedure is based upon the requirements of Standard Methods 4500-NH_3 H-97.
2. The automated phenate method is applicable to the measurement of 0.04 mg/L to 1.00 mg/L NH_3-N/L in potable and surface waters and domestic and industrial wastes. The range may be extended by diluting samples for analysis.
3. While Standard Methods states that "sample distillation is unnecessary", the method is not applicable for NPDES reporting without a preliminary distillation (40 CFR 136.3, 2012 Method Update Rule, Table IB). The same is true for all NPDES ammonia methods. Footnote 6 to Table IB indicates that distillation is not required if comparability studies indicate that distillation is not required for the test effluent.
4. ARI does not normally distill samples for ammonia analysis by either ISE or the automated phenate procedure. Clients requesting ammonia analysis by either procedure should be aware of this potential limitation in the use of the data.

2. Summary of the Procedure

1. Ammonia (NH3) in natural waters derives largely from the microbial breakdown of organic materials (deamination of organic nitrogen (R-NH2), hydrolysis of urea (H2NCONH2), etc.) and, under anaerobic conditions, the reduction of nitrate (NO3). Ammonia exists either as a dissolved gas (NH3 aq) or as the ammonium ion (NH4+), primarily dependent upon pH (temperature and dissolved solids also affect the speciation). At pH <7, NH4+ predominates and as the medium becomes more basic (pH>7) gaseous NH3 predominates (approximately 50% at pH 9 and 100% at pH>11). The approximate speciation of ammonium and ammonia is shown in figure 1 below.

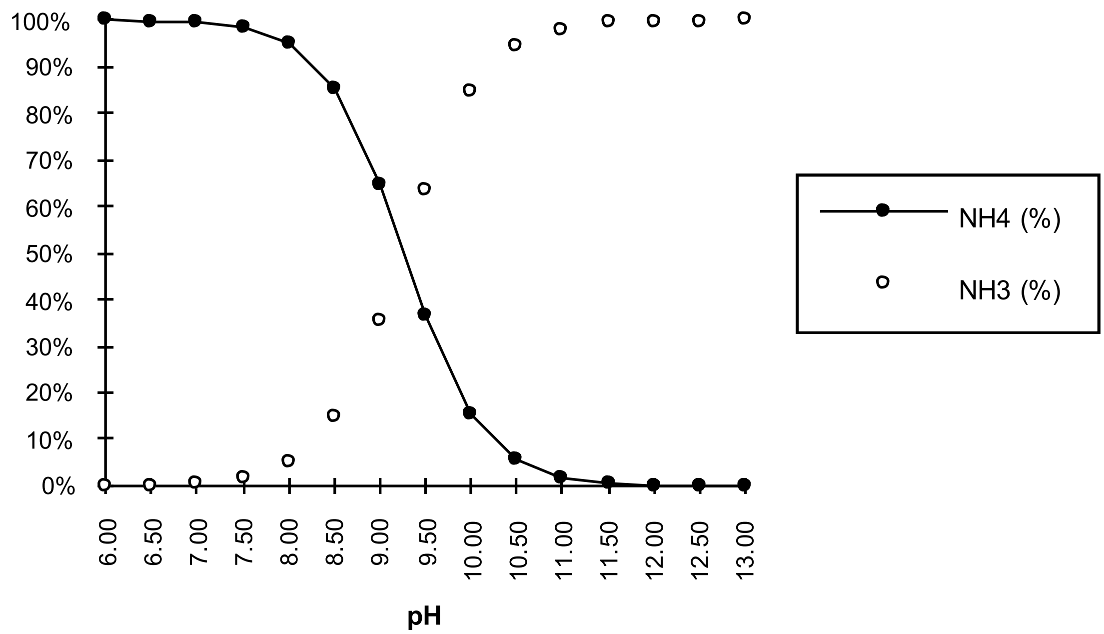


Figure 1. Approximate speciation of ammonium (NH_4) and ammonia (NH_3)

2. Two procedures are used for the analysis of ammonia in our laboratory, the automated phenate (this SOP) and ion-specific electrode (SOP ARI 616S). Both procedures measure ammonia as NH3-N under alkaline conditions. The phenate procedure allows for rapid analysis of large numbers of relatively clean low level samples (<10 mg/L) but is more subject to interference related to color, turbidity and dissolved solids. This is the procedure of choice for routine analysis. For samples which are highly turbid, colored, or have high TDS/Conductivity (>500 mg/L, >770µS) or have an ammonia concentration requiring a dilution greater than 1:100 (>100 mg/L) the ISE procedure should be used.
3. Soil/Sediment will be extracted following MSA 33.3.
   2.3.1. 1:10 Extraction with 2N KCl and a shake time of 1 hour.

3. Definitions

1. Method Detection Limit (MDL): Defined as the minimum concentration of an analyte that can be detected as being significantly greater than zero for a given instrument configuration. Defined in ARI SOP 1018S as synonymous with the Detection Limit (DL).

2. Analytical Batch: An analytical batch will consist of no more than 20 samples including one distillation blank, one Laboratory Control Standard, one Method Reporting Limit standard and matrix spikes and duplicates.
3. Method Blank (MB): The Method Blank is treated exactly the same as the samples during preparation. DI water is used for preparation of the method blank, all standards and for sample dilutions.
4. Method Reporting Limit standard (MRL): The MRL is a standard prepared at a concentration equal to the low point of the curve and treated exactly the same as the samples during preparation.
5. Laboratory Control Standard (LCS): The LCS is a standard prepared at a concentration mid-range of the curve from a secondary source and treated exactly the same as the samples during preparation.
6. Calibration Verification Standard (CVS): It is a standard prepared at a concentration mid-range of the standard curve and derived from a source other than that used for calibration. The CVS is used to verify the performance and stability of the standard curve throughout the batch run. Control limits are ±10% of the known concentration.
7. Matrix Spike (MS): A sample prepared by adding a known amount of ammonia to a specified amount of sample matrix. Matrix spikes are used to determine the effect of the sample matrix on a method's recovery efficiency.
8. Matrix Spike Duplicate (MSD): When requested will be analyzed following the MS. An MSD is required for work conducted under the Department of Defense (DoD) Quality Systems Manual. Such projects will be clearly identified by the Project Manager.
9. Matrix Duplicate: A second replicate matrix sample prepared in the laboratory and analyzed to obtain a measure of the precision of the determination with respect to the matrix.
10. Laboratory Information Management System (LIMS): Software program called Element used to track laboratory samples and produce data reports.

4. Interferences

1. Under basic conditions, NH_3 is subject to loss by volatilization hence samples are preserved by acidification which also retards microbial activity.
2. Ammonia will react with residual chlorine to form chloramines (monochloramine, dichloramine and nitrogen trichloride) hence any residual chlorine should be removed immediately upon collection.

5. Safety

1. The toxicity or carcinogenicity of each reagent used in this SOP has not been precisely defined. Treat each chemical compound as a potential health hazard. Reduce exposure to all chemicals to the lowest possible level by whatever means available.

2. Use extreme caution when handling phenol. This chemical causes severe burns and is rapidly absorbed into the body through the skin.
3. Consult the SDS for each chemical used in this procedure should questions arise. SDS are available as a hardcopy in the central office area, or online as linked on the ARI intranet.
4. Always wear appropriate PPE (personal protective equipment) when working in the Laboratory. Gloves, safety glasses, ear protection, lab coats, respirators, face shields, etc. are provided for your protection
5. Environmental Samples may contain hazardous waste; treat them as potential health hazards.
6. Concentrated acids are very dangerous. Follow proper safety procedures according to the ARI Chemical Hygiene Plan.
7. All acid and sample waste must be disposed following the ARI Waste Management Plan.
8. Dispose of all unwanted, broken glassware into a broken glassware container. Inspect every piece of glassware. Do not use any that are chipped, cracked, etched, or scratched. Glassware with minor damage should be stored for repair.

6. Equipment and Supplies

1. Lachat Quikchem® 8000 series FIA
2. XYZ Autosampler
3. Reagent Pump and associated tubing
4. Omnion Software on equipped computer and printer.
5. Volumetric Flasks
6. Pipettes
7. Analytical Balance
8. Disposable Glass Tubes, Fisherbrand Cat. No. 14-961-29

7. Reagents and Standards

1. Reagents: Use fresh deionized water (DI) when making reagents and standards. Avoid using any DI which has been stored for appreciable period of time due to the potential for ammonia absorption from the atmosphere. All reagents including DI must be degassed (unless specifically noted) with Helium at 140 kPa (20 psi) with the use of a degassing tube or a fritted glass tube. Record preparation of reagents in Element and affix labels to containers.
   7.1.1. Sodium Phenolate: CAUTION: Wear gloves. Phenol causes severe burns and is rapidly absorbed into the body through the skin. In a 1L volumetric flask, dissolve 83g crystalline phenol (C6H5OH), or 88mL of 88% liquefied phenol, in approximately 600mL DI water. While stirring, slowly add 32 g sodium hydroxide (NaOH). Cool, dilute to the mark, and invert to mix.

Do not degas this reagent. Prepare fresh every 3 to 5 days. Discard when reagent turns brown.

7.1.2. Sodium Hypochlorite: In a 500 mL volumetric flask, dilute 250 mL 5.25% sodium hypochlorite (NaOCl) to the mark with DI water. Invert to mix. Prepare fresh daily.

7.1.3. Sodium Nitroprusside: In a 1L volumetric flask dissolve 3.5g sodium nitroprusside (sodium nitroferricyanide [Na2Fe(CN)5NO.2H2O]). Dilute to the mark with DI water and invert to mix. Prepare fresh every 1 to 2 weeks.

7.1.4. 1M Sodium Hydroxide Solution: In a 1L volumetric flask dissolve 40.0 g sodium hydroxide (NaOH) in approximately 900mL DI water. Dilute to the mark and mix with a magnetic stirrer until dissolved.

7.1.5. Buffer: In a 1L volumetric flask, dissolve 50.0 g disodium ethylenediamine tetraacetic acid (Na2EDTA) and 225 mL 1 M sodium hydroxide in approximately 700 mL DI water. Dilute to the mark and mix with a magnetic stirrer until dissolved. Prepare fresh monthly.

7.1.6. 2N KCl: Partially fill a 1L volumetric flask with deionized water and dissolve 149.12g KCl. Let the reagent warm up to room temperature, then dilute to volumetric mark. Prepare fresh monthly.

2. Ammonia Standards. Ammonia standards are prepared from either ammonium chloride salt or from commercially prepared and certified reference standards. In general, the in-house prepared ammonium chloride standards will be used for preparation of standard curves and for matrix spiking. The commercially prepared standard will be used as the independent source for calibration verification. Preparation of any stock standard solution must be documented by entry of preparation data into the LIMS. You must verify that data entry is correct and that ammonia is expressed as elemental nitrogen (i.e. NH3-N). All standards must be made volumetrically using clean volumetric glassware and pipettes.

7.2.1. Ammonium chloride Stock standard (1,000 mg NH3-N/L). In a 1 liter volumetric flask dissolve 3.8189 g anhydrous ammonium chloride (NH4Cl, FW = 53.492, 26.18%N), pre-dried at 100 ºC, into approximately 500 mL fresh DI and dilute to 1000 mL. Enter data (exact weight and volume) into LIMS and print a label for the prepared bottle to show the name of the standard, the standard ID Number, the date of preparation and your initials. Use this standard for the preparation of the Intermediate ammonia standard and prepare fresh annually or as needed.

7.2.2. Intermediate NH3-N Standard (Concentration = 20 mg/L). Dilute 2 mL of the NH3-N Stock standard to 100 mL with DI. Use this solution for the preparation of the Standard Curve. Prepare this Intermediate Standard weekly.

3. Calibration Standards. Dilute the above Intermediate Standard to 100 mL as indicated in the table below: These standards must be made fresh weekly and should be labeled with the date of preparation and your initials.

Standard #	Final volume (mL)	Volume of Intermediate Std (20 ppm) (mL)	Concentration (mg/L NH_3-N)
S0	100	0.0	0.0
S1	100	0.20	0.04
S2	100	0.50	0.10
S3	100	1.00	0.20
S4	100	2.50	0.50
S5	100	4.00	0.80
S6	100	5.00	1.00

4. Method Blank. The Method Blank for preserved samples is prepared by adding 2 mL 9N H2SO4 to a 500 mL sample bottle containing DI. The method blank is used to prepare the MRL and LCS. For unpreserved samples the method blank is a DI filter blank. Prepare fresh with each batch.
5. Method Reporting Limit standard (MRL). The MRL is prepared at the low point of the curve by diluting 0.1 mL 20 ppm intermediate to 50 mL with the method blank. Prepare fresh with each batch.
6. Laboratory Control Standard (LCS). The LCS is prepared from a 1000 mg/L NIST traceable independent source stock solution. Dilute 0.05 mL of the 1000 mg/L stock to 100 mL using the method blank for a concentration of 0.50 mg/L. Prepare fresh with each batch.
7. Calibration Verification Standard (CVS). Calibration verification standard is prepared from a 1000 mg/L NIST traceable independent source stock solution. To prepare the working standard add 0.05 ml of the 1000 mg/L stock to a 100 mL volumetric flask containing about 50 mL of DI. Mix well and bring to a 100mL final volume, the concentration is 0.50 mg/L. This standard should be prepared weekly.

8. Sample Collection, Preservation, Shipment and Storage

1. Aqueous samples are collected in 500 ml HDPE containers, preserved with 9N H2SO4 to pH <2 and kept cool between 0 – 6 degrees C. Preserved samples can be held up to 28 days, but unpreserved samples must be analyzed within 48 hours from collection.
2. Solid samples are collected in 4 oz wide mouth glass jars and kept cool between 0 – 6 degrees C. The holding time for solid samples is 7 days.

9. Quality Control

1. Demonstration of Capability. Each analyst using this procedure must run an initial "Demonstration of Capability" by preparing and analyzing 4 replicates of the QC Check Solution. The recovery (Accuracy) must be within the range of ±10 % (90 to 110 %) with a relative standard deviation (Precision) less than 10 %. An on-going DOC will be provided by the analysis and recording of the QC Check Solution for each batch of ammonia analyses conducted.
2. Detection and quantitation limits are retained in LIMS. See SOP 1018S for additional information on how detection and quantitation limits are calculated.
3. Control charts for trend analysis. Control charts for the Ammonia Low Level Check Standard will be constructed and updated on a periodic basis. Results will be evaluated relative to Warning and Control limits set at 2 and 3 standard deviations of the mean, respectively.
4. The regression coefficient, r should be greater than 0.995.
5. Initial Calibration Verification (ICV) and Calibration Blank (ICB) must be run at the beginning of each batch. Continuing Calibration Verification standards and blanks (CCV, CCB) must be run after every ten samples in the batch and at the end of each run. The calibration verification standards must agree within ±10% of the "true" value and the concentration of the blanks should be less than the absolute value of the reporting limit.
6. Matrix spike and duplicate analyses are run with each batch or as requested by the client.
   - 9.6.1. Duplicate analysis. If both the original and duplicate sample concentrations are greater than 5X the detection limit, the calculated RPD should be less than 20%. If either concentration is less than 5X the detection limit, then the absolute difference between the two should be less than or equal to the detection limit. If these criteria are not satisfied, corrective actions must be taken.
   - 9.6.2. Matrix Spikes. The acceptance limits for matrix spike recoveries are ±25% if the original concentration is less than 4X the spike concentration added. If the original concentration is greater than 4X the added spike level, the spike is invalid and must be repeated.
7. MRL Check Standard: A standard prepared at the low point of the curve and prepared exactly the same as the samples on the batch. Run immediately following the ICV/ICB.
8. Method Blank: A method blank should be analyzed with each batch after the MRL Standard. This blank should have a value less than the absolute value of the reporting limit.
9. Laboratory Control Standard: A positive control standard prepared with each batch. The LCS must agree within ±10% of the "true" value.

10. Calibration and Standardization

1. A six point calibration curve is prepared weekly, ranging from 0.04 to 1.0 mg/L NH_3-N, and analyzed with each sequence.

2. Initial Calibration Verification (ICV) and Calibration Blank (ICB) are run at the beginning of each sequence. Continuing Calibration Verification standards and blanks (CCV, CCB) are run after every ten samples in the sequence and at the end of each run.

11. Procedure

1. Preparations
   - 11.1.1. If residual chlorine is suspected use Starch-Potassium Iodide paper to test the sample. If detected it can be removed by adding 1 mL of sodium thiosulfate solution (0.35 grams sodium thiosulfate dissolved in 100 mL DI) to 500 mL of sample. Retest for residual chlorine and add additional reagent as necessary. If present and sample treatment was required, document on the Analyst Notes “Green Sheet”.
   - 11.1.2. Preserved samples should be neutralized before analysis. Adjust samples and batch standards to pH 5-9 with either 6.0 M NaOH or 1+1 H2SO4.
2. Operating Procedure (Lachat):
   - 11.2.1. Basic Operation and Maintenance of the Lachat is more detailed in SOP 659S, Lachat Instrument Basic Operation and Data Management. Analysts should also consult the Lachat instrument user guides.
   - 11.2.2. Note: NH3 is a heated chemistry. The manifold tubing is attached to the heater after the last ‘T’ and just prior to the flow cell/detector. To eliminate the possibility of reagents sitting in the tubing, while the heater in on in stand by mode, switch the pump to “MANUAL”.
   - 11.2.3. Turn on the power to the autosampler, pump and system unit along with the associated computer and printer. Switch the pump to “MANUAL”. Note: Prior to running, perform any required maintenance as outlined in the instrument maintenance log. Document the maintenance performed.
   - 11.2.4. Open OMNION 3.0 software displayed as an icon on the system computer desktop.
   - 11.2.5. Method parameters and conditions including timing, designated pump tubing, sample loop size etc. are already defined within the system and should not be modified without consultation with Conventionals lab supervisor and adequate documentation. Refer to the appendices for the manifold diagram and system parameters.
   - 11.2.6. Select ‘Run’, ‘Open’ in the toolbar.
   - 11.2.7. Choose appropriate ammonia template from the available files (e.g. NH3.omn) Note: Ensure that proper calibration standard values appear for each corresponding standard ID. Verify ICV/CCV (Sample type = ‘Check Standard’) concentration is correct.
   - 11.2.8. Enter batch QC and sample ID’s starting in the cell following the ICB. Sample Type = “Unknown”.

11.2.9. Enter CCV (Sample Type = "Check Standard")/CCB after every 10 injections including rinse blanks. Enter 0.5 ppm known concentration and ±10% acceptance criteria for the CCV and 0ppm known concentration and ±MRL acceptance criteria for the CCB. Schedule these as a Data Quality Management (DQM) set to be run after every 10 injections and at the close of the run.

11.2.10. Add lines in the sample tray template as needed for samples and QC. Note: CCV's and CCB's will be automatically entered into the tray at the required interval when defined as a DQM set. Adjust the cup numbers to correspond with sample tube placement in the autosampler rack.

11.2.11. Record the entries of the sample tray in the Lachat Run Log.

11.2.12. Filter all samples including the batch QC standards using a 20mL disposable syringe and 0.45µm syringe filters. One filter per sample and rinsing the syringe three times with DI water between samples.

11.2.13. Sample duplicates need to be analyzed for each batch of samples.

11.2.14. Matrix spikes are prepared at a 0.5 ppm concentration if QC limits stated in Section 9.6.2 are met. For samples requiring dilution the sample is first spiked with standard and then the dilution performed on the 10 mL final volume of spiked sample. "Spike first, then dilute". Add the appropriate spike as stated in the table below and take to a 10 mL final volume with filtered sample, then dilute. Spiking guidelines are as follows:

Required sample dilution	**mL Intermediate Standard (20ppm)**	**mL of Stock Standard (1000ppm)**	**Final volume of spiked sample**
Undiluted	0.250		10mL
1:5		0.025	10mL
1:10		0.05	10mL
1:20		0.10	10mL
1:50		0.25	10mL
1:100		0.50	10mL

11.2.15. Load the sample tubes in the exact sequence as indicated in the sample table. **Note**: Samples are loaded and run starting in the lower left-hand corner of the rack and continuing up then starting again at the bottom of the next column. Calibration standards are loaded highest to lowest concentration ending with the blank.

11.2.16. Observe pump tubing and manifold lines for jerky motion that indicates a flow problem and/or backpressure. Also check for any leaks at all tees and junctions. Refer to the troubleshooting section of the User's manual if problems are noted.

11.2.17. If no flow problems are apparent transfer reagent pump tubing from the DI water to the appropriate reagent containers. Continue pumping (pump speed at 35) until air bubbles are removed and baseline is void of air spikes and appears steady with no drift upward or downward. (Press ‘Preview’ on the toolbar to monitor current baseline.)

11.2.18. Press ‘Start’ on the toolbar to begin the run. Note: Calibration is run first and upon passing the samples will be analyzed. The methods have been set to halt the tray if the r<0.995.

11.2.19. Review the calibration while samples are running and note the peak area of the 1.0 ppm standard. Peak area should be approximately 35-40 V-s (volt-seconds). If this value falls outside this range, the run should be stopped and the cause of the peak area change should be determined. Refer to the User’s manual for troubleshooting guidelines.

11.2.20. Save the run as MMDDYYXXXS.omn where M is a 2 digit code for the month, D is the 2 digits for the day, YY is the 2 digits for the year, X is the 3 letter code for the parameter, S is the sequence letter for the day’s runs and ‘omn’ is the required filename extension needed for the Omnion software to recognize the file. Press ‘Enter’. For example, if this is the second Lachat run conducted on February 5, 2004 the file name would be: 020504NH3B.omn.

11.2.21. To generate the final report for the run go to ‘Tools’ in the toolbar, ‘Custom Report’. Click the Format icon.

11.2.21.1. Under the Table tab de-select ‘Rep #’, select ‘Detection Time’, ‘Cup #’, ‘Peak Area’ and ‘Manual Dilution Factor’ if the manual dilution factor was entered in the sample table prior to the sample running.

11.2.21.2. Under the Layout tab enter your initials in the ‘Author’ portion of the Header box and the filename and instrument name in the Right portion of the Footer box.

11.2.21.3. Under the Charts tab in the Options section select ‘Calibration’ and select Channel Data Display. Then select ‘Show 10 Peaks per Chart for All Peaks’.

11.2.22. Click ‘Apply’ to incorporate all chosen options to the report then ‘Close’.

11.2.23. Evaluate all results for the run including: Regression coefficient (r), calibration standard regressed values, initial calibration blank (ICB), initial calibration verification (ICV), batch QC standards, continuing calibration blanks and checks (CCB, CCV), RPD, matrix spike recovery and any off scale samples. If some of these parameters are out of the range, re-run the affected samples. IT IS THE RESPONSIBILITY OF THE ANALYST TO VERIFY ALL DATA.

11.2.24. Print out the final report.

11.2.25. At the end of the day’s analysis. Turn off the heating coil. Place the transmission lines in cleaning buffer (65 g NaOH and 6 g tetrasodiumethylenediamine tetraacetic acid (EDTA) dissolved in 1 L DI water) and pump through the manifold for 10 minutes. After 10 minutes place the transmission lines in DI water and pump water through for 10 minutes. After the water rinse remove the transmission lines from the water and pump the manifold dry.

11.2.26. Stop pump and remove lines from the pump cartridges. Turn off the power to the autosampler, pump, and system. Turn off computer.

11.2.27. Wipe down all instrument surfaces and wash pump cartridges. Record maintenance in the instrument maintenance log.

3. Operation Notes:

11.3.1. Staining of the pump tubing

11.3.1.1. Ensure the mixed stream between the last tee and the heater is between pH 11 and 12. Higher than 12.3 (usually caused by too much NaOH in the buffer) will contribute to staining.

11.3.1.2. Crystalline phenol is preferred over liquid or solid. The reagent needs to be prepared at least every 3-5 days, sooner if the color turns darker than pale orange.

11.3.1.3. Do not allow the pump to go to STANDBY mode.

11.3.2. Negative peaks

11.3.2.1. This can occur if the carrier and sample matrices are different. For best results neutralize the samples to a pH of 6-9 prior to running and use the non-acidified reagents.

11.3.2.2. Ammonia contamination of the carrier can produce negative peaks. Use fresh DI water and keep covered to prevent ambient ammonia contamination.

11.3.2.3. High metals concentrations within samples will precipitate and create negative peaks. Samples with this characteristic should be diluted to reduce the metals effect.

11.3.3. For high concentration samples, samples requiring >100X dilution, ion specific electrode (ISE) is the preferred method. See the NH3-ISE SOP for details.

11.3.4. Use the KCl extraction procedure for the analysis of soil and sediment samples. See the NH3-ISE SOP for details on the procedures for soils extraction.

12. Review

1. Refer to ARI's Laboratory Quality Assurance Plan for data review procedures.
2. Specifically for Ammonia, the analyst should check instrument output for accuracy and examine chromatograms to ensure all reported peaks are correctly integrated. Any anomalies such as abnormal peak shapes should be recorded in the analyst comments.

13. Data Analysis and Calculations

1. Calibration is done by injecting standards. The data system prepares a calibration curve by plotting response versus standard concentrations. Sample concentration is calculated from the regression equation.

2. Report only those values that fall between the lowest and highest calibration standards. Samples exceeding the highest standard should be diluted and reanalyzed.

14. Method Performance

1. The reporting limit is set to the lowest calibration curve standard at 0.04 mg/ L NH_3-N.

15. Pollution Prevention

1. Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation.
2. The quantity of chemicals purchased should be based on expected usage during their shelf life to reduce disposal cost of unused material. Actual reagent preparation volumes should reflect anticipated usage and reagent stability.

16. Data Assessment and Acceptance Criteria for QC Measure

1. The regression coefficient, r should be greater than 0.995.
2. The calibration verification standards must agree within ±10% of the "true" value and the concentration of the blanks should be less than the absolute value of the reporting limit.
3. If both the original and duplicate sample concentrations are greater than 5X the reporting limit, the calculated RPD should be less than 20%. If either concentration is less than 5X the reporting limit, then the absolute difference between the two should be less than the reporting limit. If these criteria are not satisfied, corrective actions must be taken.
4. Matrix Spikes. The acceptance limits for matrix spike recoveries are ±25% if the original concentration is less than 4X the spike concentration added. If the original concentration is greater than 4X the added spike level, the spike is invalid and must be repeated.
5. The LCS must agree within ±10% of the "true" value.
6. The method blank should have a value less than the absolute value of the reporting limit.

17. Corrective Actions for Out of Control Events

1. If r is less than 0.995, new calibration standards must be prepared and the calibration repeated. All samples associated with the out of control standard curve must be re-run.
2. If Initial Calibration Verification (ICV) and Initial Calibration Blank (ICB) are out of QC limits, new calibration standards or new ICV solution should be made. All samples associated with the out of control condition must be re-run. If the Continuing Calibration Verification (CCV) and Continuing Calibration Blank (CCB) are out of QC limits, they should be reread to verify. All samples between the last in control condition and the out of control condition must be re-run. All samples in any run must be bracketed by in control verification standards.

3. After the above two corrective actions, if the results are still outside the limits, the supervisor will review the entire procedure with the analyst to verify that correct procedures are being followed or check the instrument to make sure it is working properly.
4. If the method blank or LCS is out of control, it should be reread to verify. If the results are still out of control, stop the run and evaluate the filters and procedure. All samples on the batch will need to be re-filtered and reanalyzed. If results are persistent it may be required that each filter first be rinsed with DI water then with sample before filtering the portion used for analysis.
5. If RPD or matrix spike recoveries are outside the prescribed limits, the analysis will be repeated to confirm the outlying condition.
6. If any of the following situations arises, the supervisor will be immediately notified and the project manager will be informed for resolution with the client:
   - 17.6.1. Samples have exceeded holding times.
   - 17.6.2. Samples have been improperly preserved.
   - 17.6.3. There is insufficient sample to run the analysis.
7. Analyst's notes are recorded on the Analyst's Notes ("green sheet") in the job folder. Sample anomalies such as unusual sample characteristics or sample problems that were not covered on a Corrective Action form are recorded here.
8. As a general rule, all corrective actions taken during the course of an analysis must be described on the analysts comment sheet (i.e. the green sheet) and a Corrective Action Sheet must be submitted to the PM. It must be clearly evident to the data reviewer and PM exactly how a sample was handled during analysis.

18. Contingencies for Handling Out-of-Control or Unacceptable Data

1. Any out-of-control events (i.e. failed spike, high RPD, failed CCV) will be noted on a Corrective Action form including the recommended corrective action and corrective action taken. The form is generated and completed by the analyst. It is turned in for review with the affected data and signed by the supervisor.
2. Analyst's notes are recorded on the Analyst's Notes ("green sheet") in the job folder. Sample anomalies such as unusual sample characteristics or sample problems that were not covered on a Corrective Action form are recorded here.

19. Waste Management

1. The phenol hypochlorite waste generated as a result of this analysis is considered a hazardous waste mixture for the characteristic of toxicity (phenol in excess of 1%). These wastes must be collected during the run and transferred to the phenol/ammonia waste accumulation container located in the laboratory.

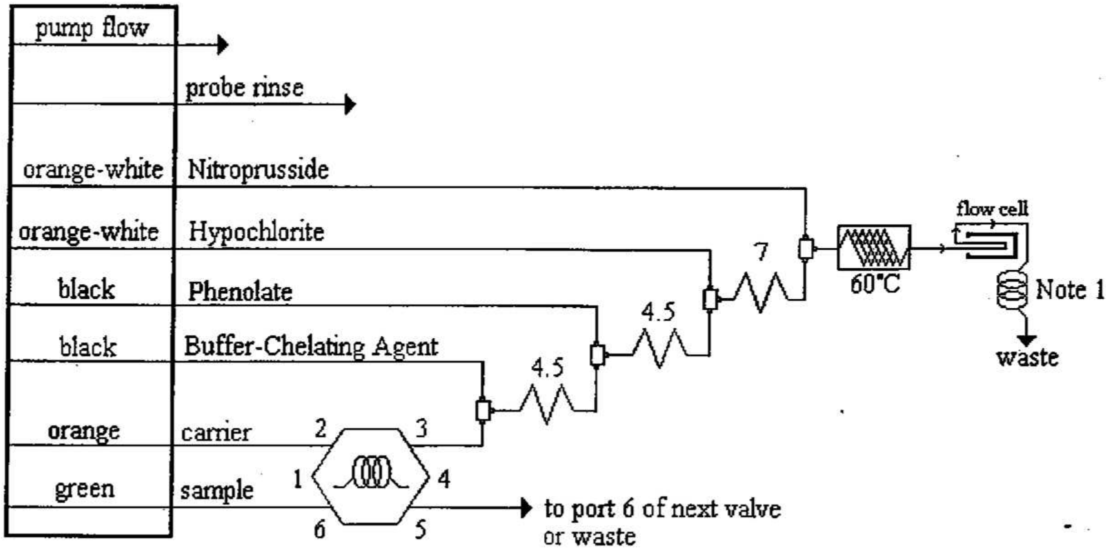
2. Analysis waste is collected under the rules of Satellite Accumulation at the site of generation and under the control of the operator of the process generating the waste. When the waste container is full it is transferred to the Central Accumulation Area.

20. Method References

1. Standard Method for the Examination of Water and Wastewater. 1997. 20th ED. Method 4500–NH3 H.
2. Methods for Chemical Analysis of water and wastes. EPA-60014-79-020 (Rev 2, August 1993). Method 350.1.
3. 40 CFR Part 136, Guidelines Establishing Test Procedures for the Analysis of Pollutants, Table II, Required Containers, Preservation Techniques, and Holding Times.
4. 40 CFR Part 136, Guidelines Establishing Test Procedures for the Analysis of Pollutants, Appendix B. Definition and Procedures for Determining the Method Detection Limit
5. Keeney and Nelson. 1987. Nitrogen, Inorganic Forms. 33-3. Extraction of Exchangeable Ammonium, Nitrate, and Nitrite. Methods of Soil Analysis, Part 2. Chemical and Microbiological Properties - Agronomy Monograph no. 9 (2nd edition)

21. Appendices

1. Ammonia Manifold Diagram



Carrier: **DI water**
Manifold Tubing: **0.5 mm (0.022 in) i.d.** This is **2.5 µL/cm**.
AE Sample Loop: 125 cm x 0.022 in. i.d.
QC8000 Sample Loop: 125 cm x 0.022 in. i.d.
Interference Filter: 630 nm

Apparatus: An injection valve, a 10 mm path length flow cell, and a colorimetric detector module is required. The [heater symbol] shows 650 cm of tubing wrapped around the heater block at the specified temperature.

4.5: **70** cm of tubing on a 4.5 cm coil support
7: **135** cm of tubing on a 7 cm coil support
8: **168** cm of tubing on a 8 cm coil support
12: **255** cm of tubing on a 12 cm coil support
22: **550** cm of tubing on a 22 cm coil support

Note 1: 200 cm backpressure loop (0.022 in. i.d.)
Note 2: PVC PUMP TUBES MUST BE USED FOR THIS METHOD

2. Data System Parameters

21.2.1. Analyte Data:

21.2.1.1. Pump Speed:	35
21.2.1.2. Cycle Period:	65
21.2.1.3. Concentration units:	mg NH3-N/L
21.2.1.4. Sample Period:	30 s
21.2.1.5. Inject to Peak Start:	80 s
21.2.1.6. Chemistry:	Direct

21.2.2. Calibration Data:

21.2.2.1. Calibration Rep Handling:	N/A
21.2.2.2. Calibration Fit Type:	1st Order Polynomial
21.2.2.3. Weighting Method:	None
21.2.2.4. Force through zero:	No

21.2.3. Sampler Timing:

21.2.3.1. Min. Probe in Wash Period:	12 s
21.2.3.2. Probe in Sample Period:	32 s

21.2.4. Valve Timing:

21.2.4.1. Time to Valve:	24 s
21.2.4.2. Load Period:	28 s
21.2.4.3. Inject Period:	37 s

The State of Washington
Department of Ecology

Materials Testing & Consulting, Inc - Olympia
Olympia, WA

has complied with provisions set forth in Chapter 173-50 WAC and is hereby recognized by the Department of Ecology as an ACCREDITED LABORATORY for the analytical parameters listed on the accompanying Scope of Accreditation.

This certificate is effective March 26, 2020 and shall expire March 25, 2021.

Witnessed under my hand on March 05, 2020.

Rebecca Wood
Lab Accreditation Unit Supervisor

Laboratory ID
C1041

WASHINGTON STATE DEPARTMENT OF ECOLOGY

ENVIRONMENTAL LABORATORY ACCREDITATION PROGRAM

SCOPE OF ACCREDITATION

Materials Testing & Consulting, Inc - Olympia

Olympia, WA

is accredited for the analytes listed below using the methods indicated. Full accreditation is granted unless stated otherwise in a note. EPA is the U.S. Environmental Protection Agency. SM is "Standard Methods for the Examination of Water and Wastewater." SM refers to EPA approved method versions. ASTM is the American Society for Testing and Materials. USGS is the U.S. Geological Survey. AOAC is the Association of Official Analytical Chemists. Other references are described in notes.

Matrix/Analyte	Method	Notes
Solid and Chemical Materials		
Particle Size Distribution	ASTM D422	1
Particle Size Distribution	PSEP 1995 (Puget Sound Estuary Protocols)	1

Accredited Parameter Note Detail

(1) Interim accreditation pending the successful completion of an on-site audit to verify method capabilities (WAC 173-50-100).

Rebecca Wood

Authentication Signature
Rebecca Wood, Lab Accreditation Unit Supervisor

03/05/2020

Date